



# Nontargeted LC-MS Analysis of Next-Generation PFAS in New Jersey Soil and Vegetation

Mary J. B. Davis

U.S. Environmental Protection Agency

Waters Southeast Mass Spectrometry Users Meeting

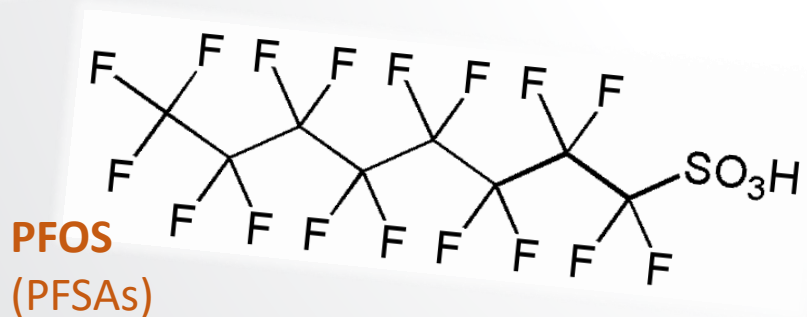
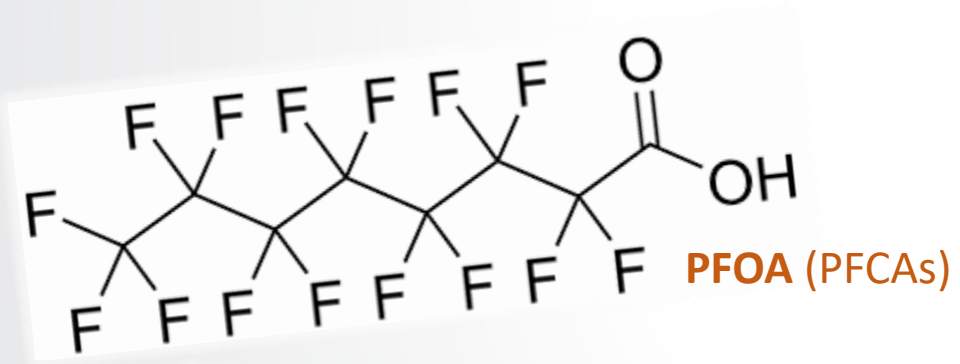
July 21, 2020

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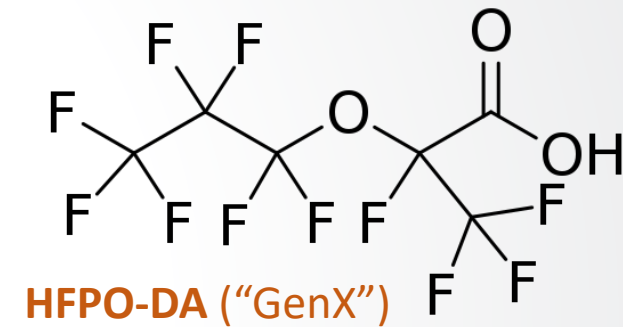
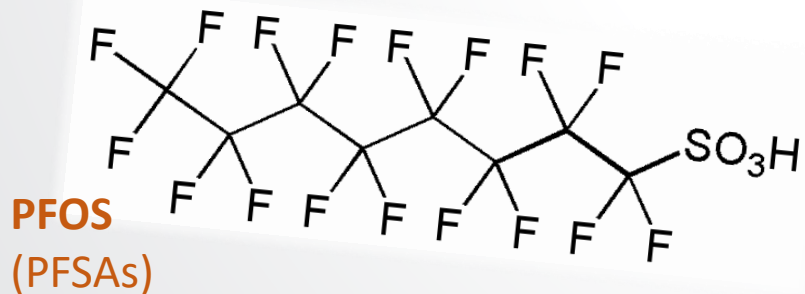
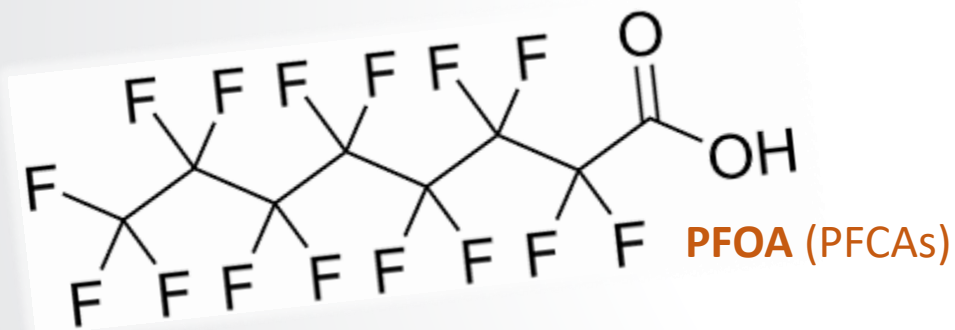
# Expansion of PFAS

- Longer-chain legacy PFAS have largely been phased out of production in the United States



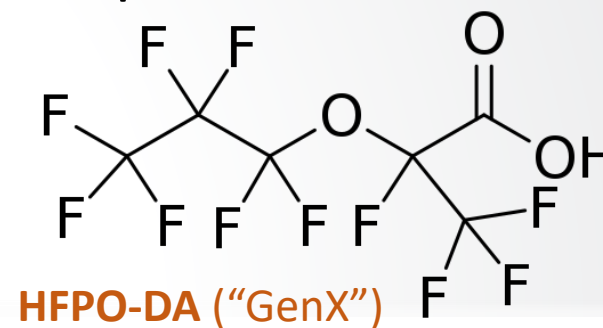
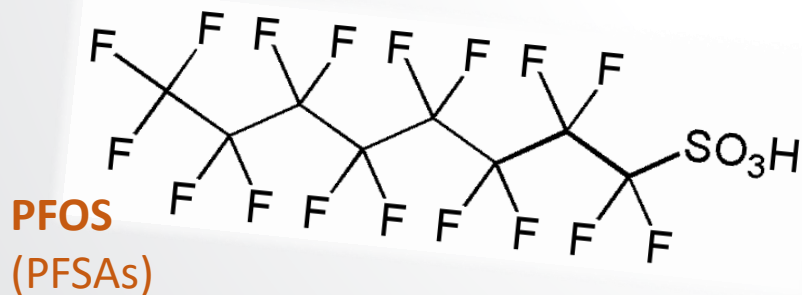
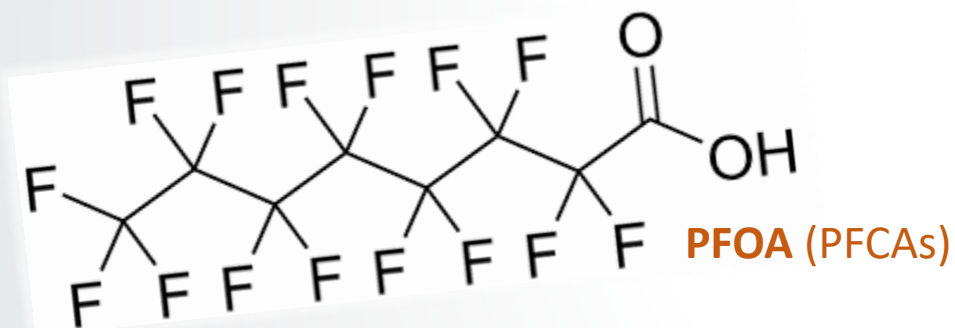
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# Expansion of PFAS

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**Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater**

Krista A. Barzen-Hanson,<sup>†</sup> Simon C. Roberts,<sup>‡</sup> Sarah Choyke,<sup>§</sup> Karl Oetjen,<sup>‡</sup> Alan McAlees,<sup>||</sup> Nicole Riddell,<sup>||</sup> Robert McCrindle,<sup>‡</sup> P. Lee Ferguson,<sup>§</sup> Christopher P. Higgins,<sup>\*,‡</sup> and Jennifer A. Field<sup>\*,#</sup>

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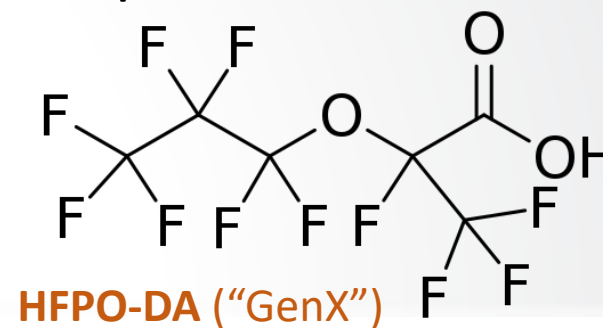
Cite This: *Environ. Sci. Technol.* 2019, 53, 4717–4727

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  - Continuous industrial development



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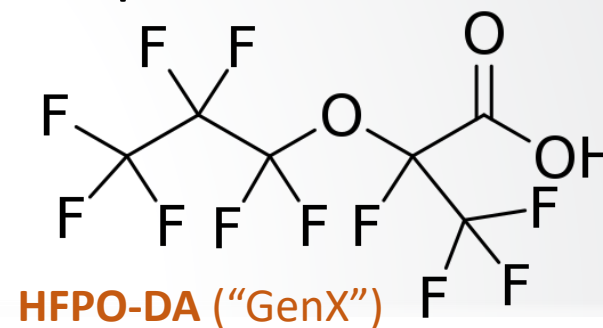
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- “Next-generation” replacement PFAS
- Challenges:
  - Availability of standards
  - Continuous industrial development

**Nontargeted Analysis enables discovery of these new compounds and directs future research efforts**



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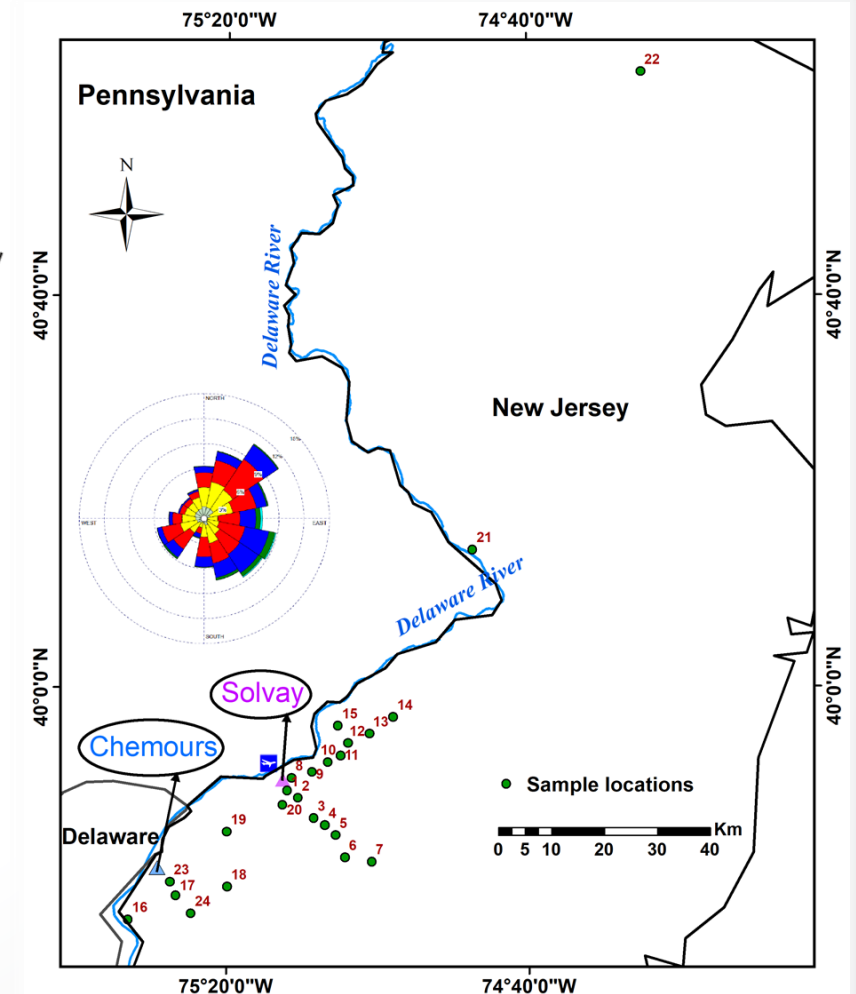
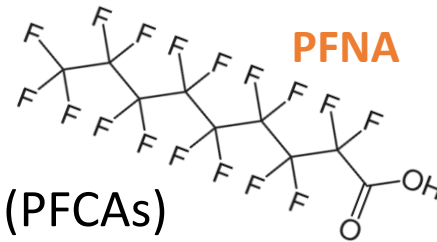
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# Looking for PFAS in Environmental Samples in NJ

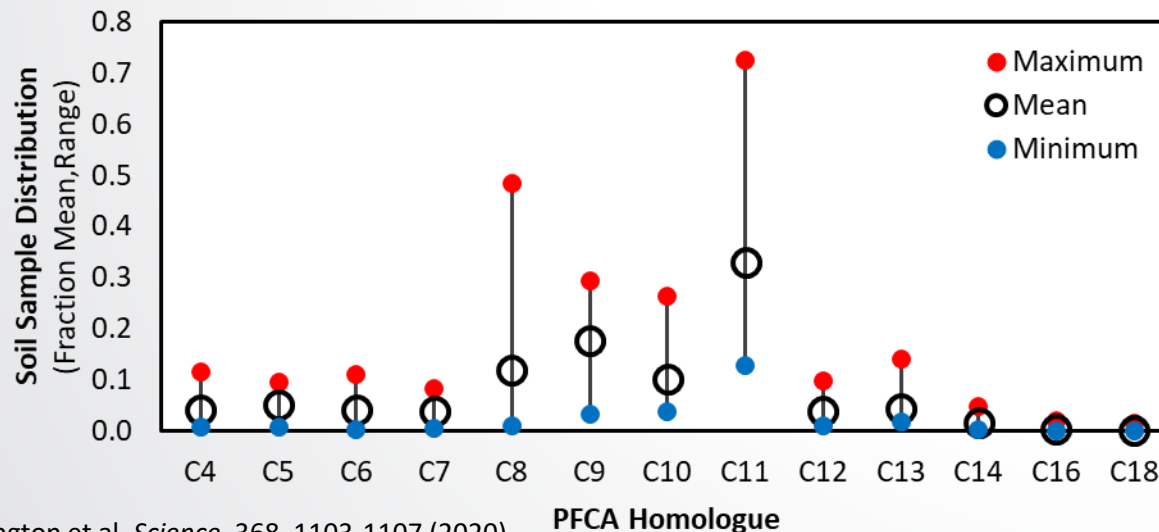
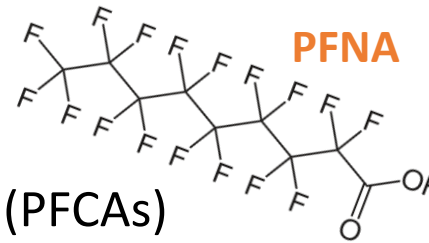
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- Targeted analysis for perfluorocarboxylic acids (PFCAs) indicated presence at ppt-ppb levels



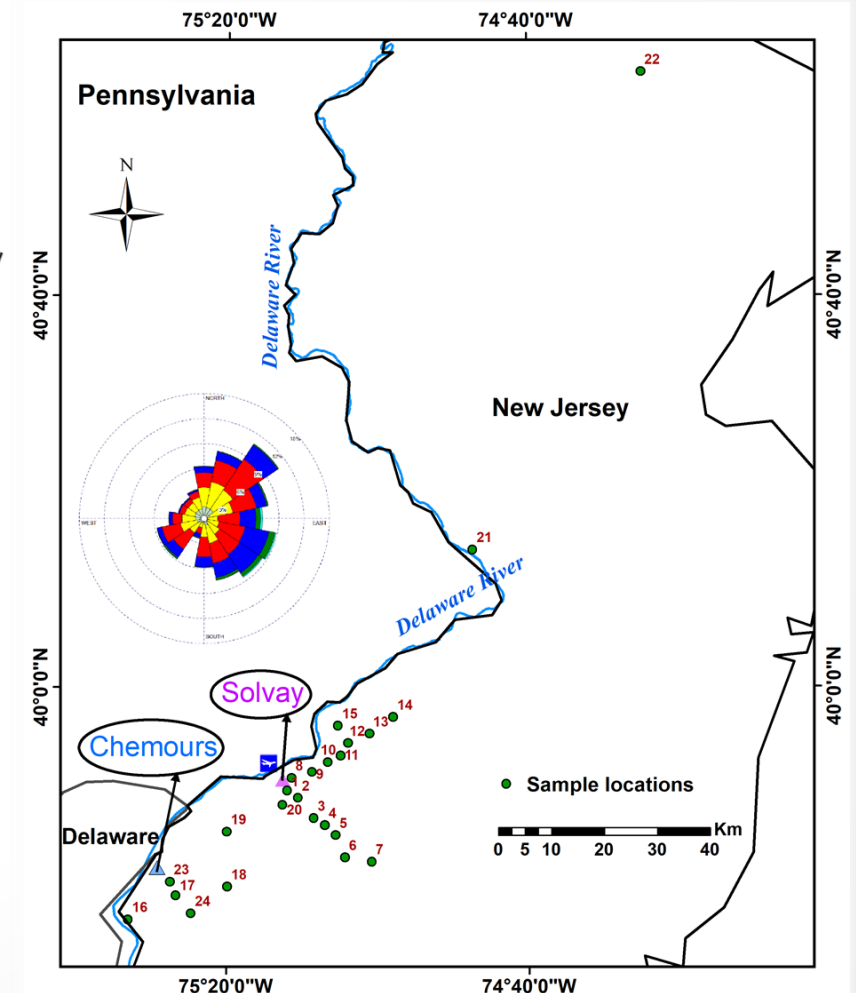
NJ soil and vegetation sampling sites



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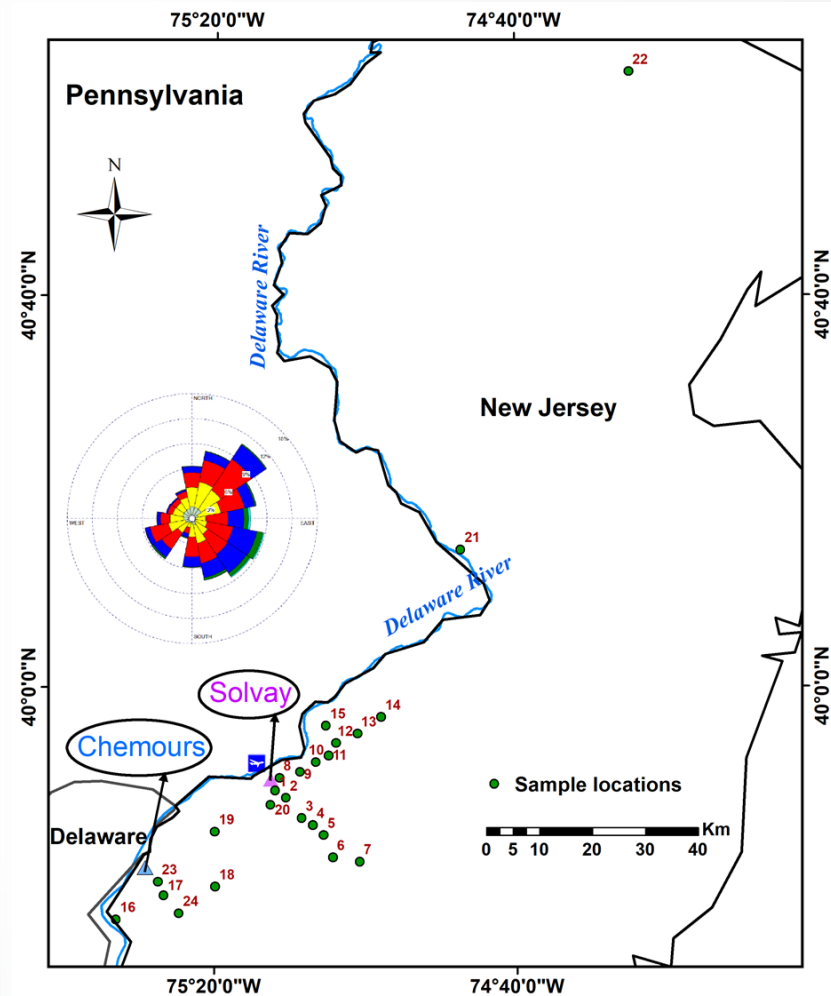
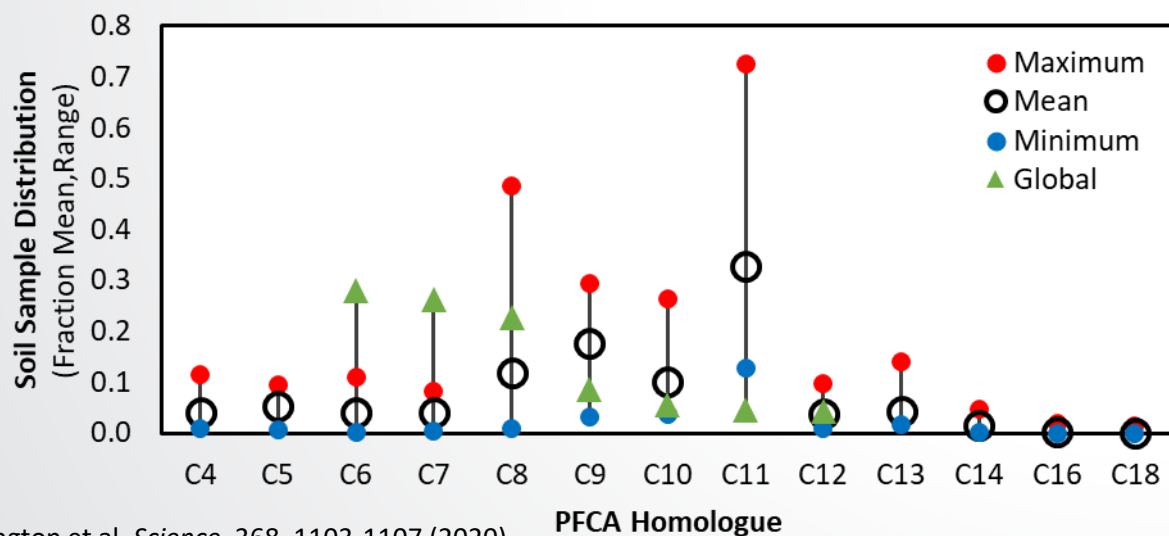
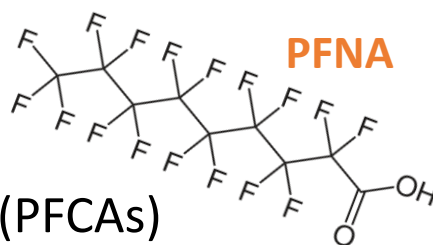
Washington et al. *Science*, 368, 1103-1107 (2020).



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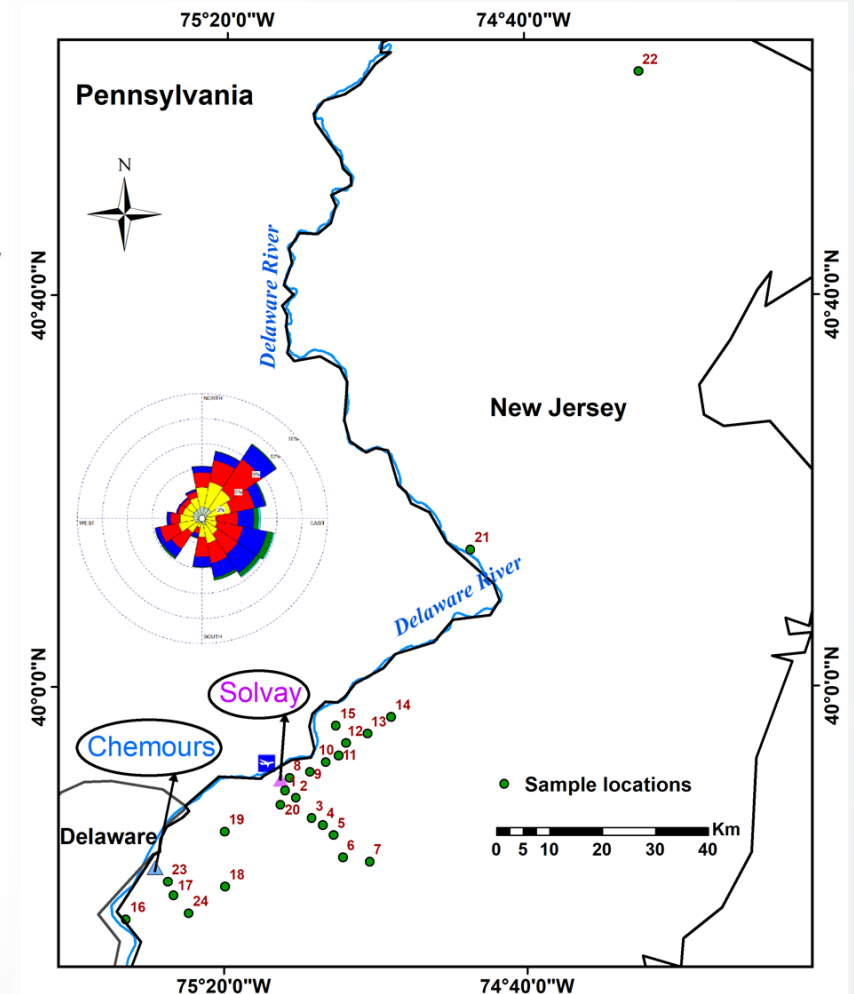
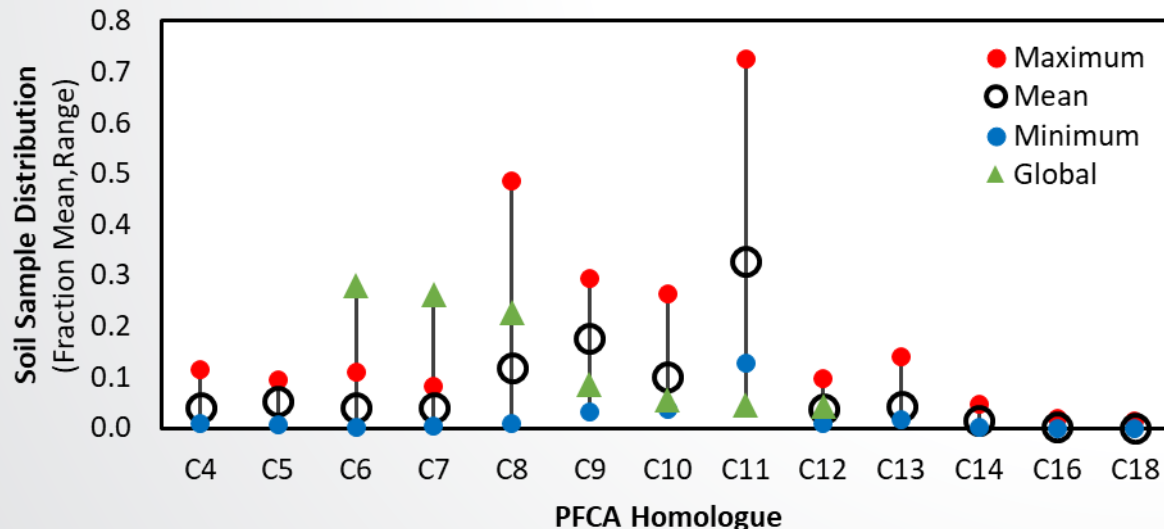
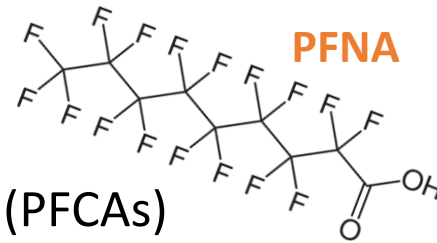


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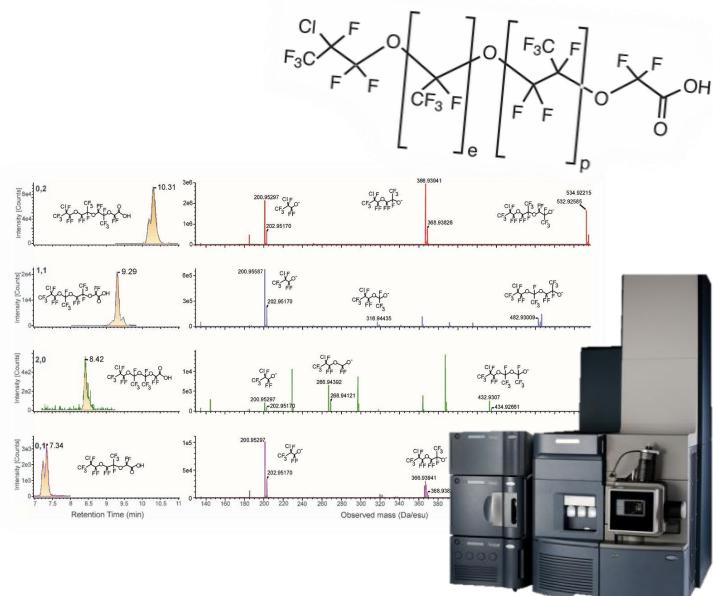
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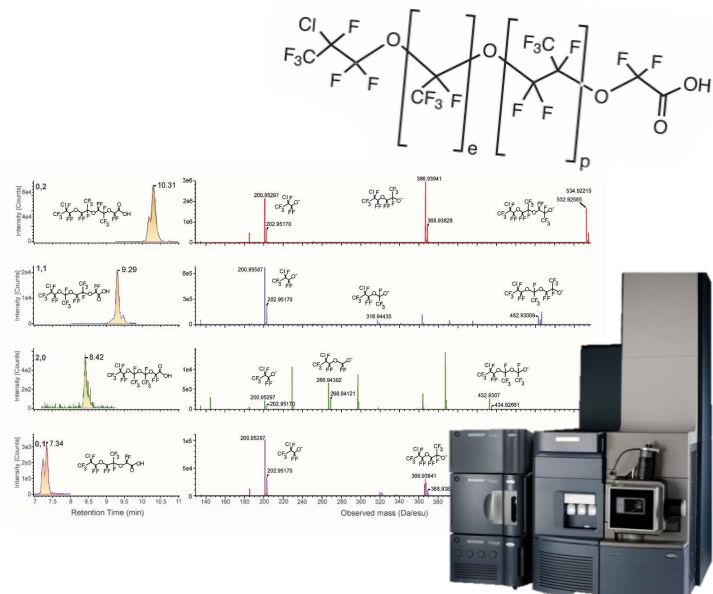
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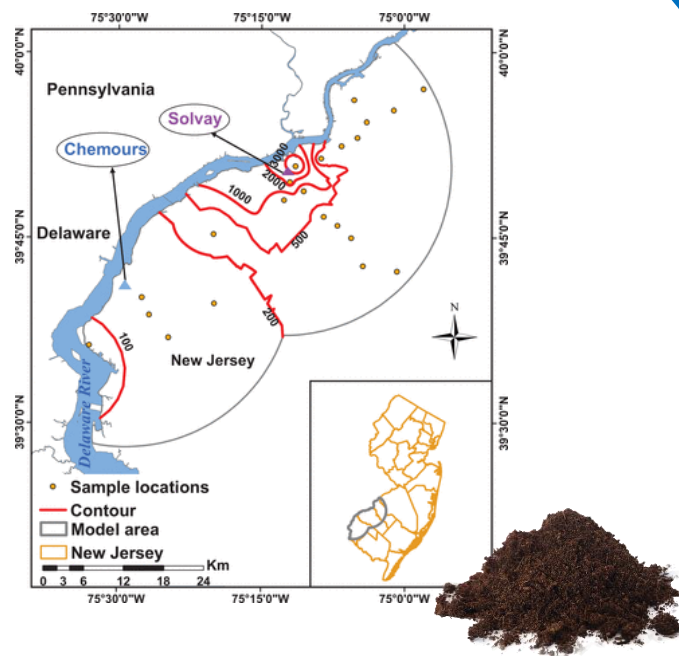
# Nontargeted Analysis of PFAS in Environmental Samples



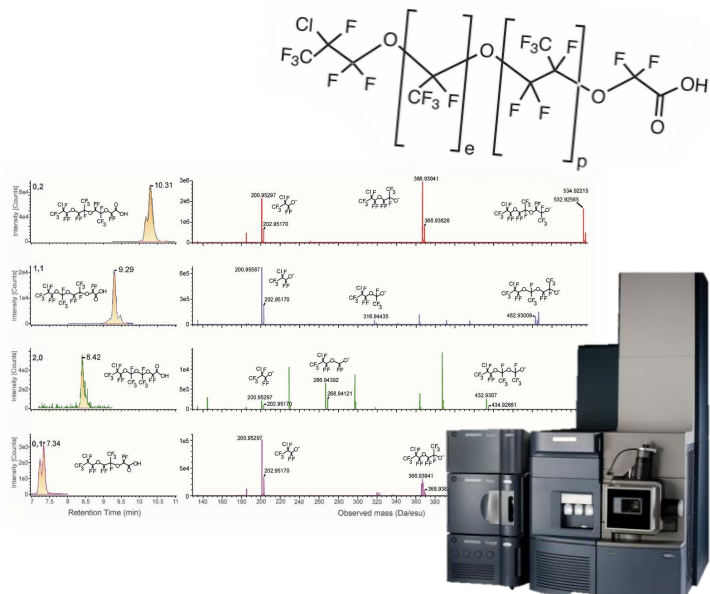
Method for detecting the presence of next-generation PFAS in NJ environmental samples via nontargeted analysis



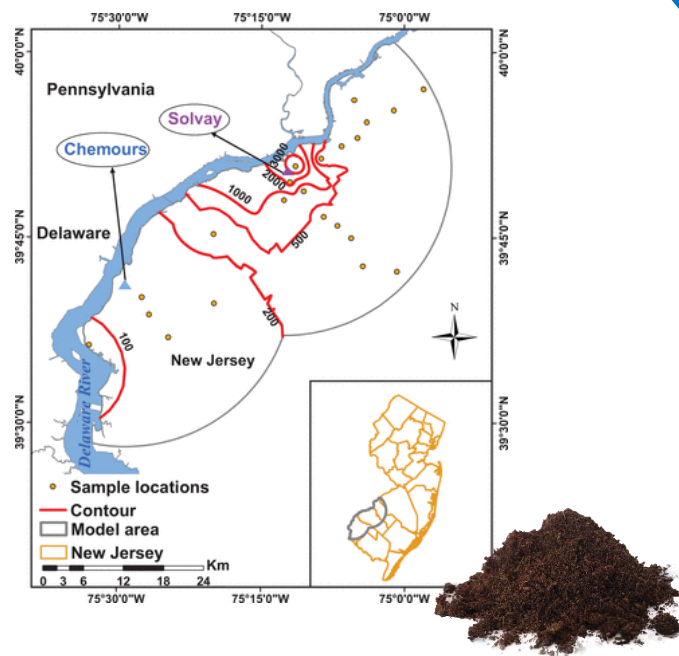
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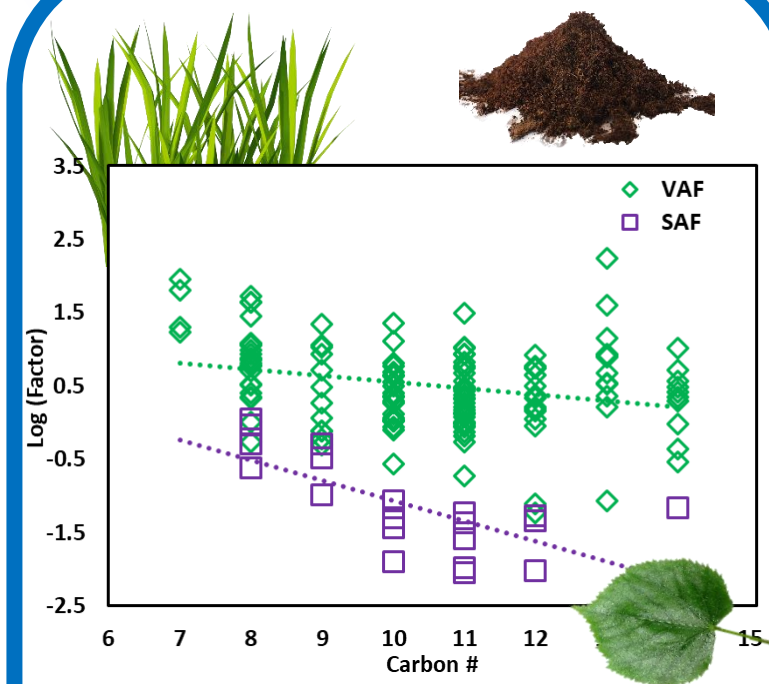
Semi-quantitation of compounds for environmental source analysis



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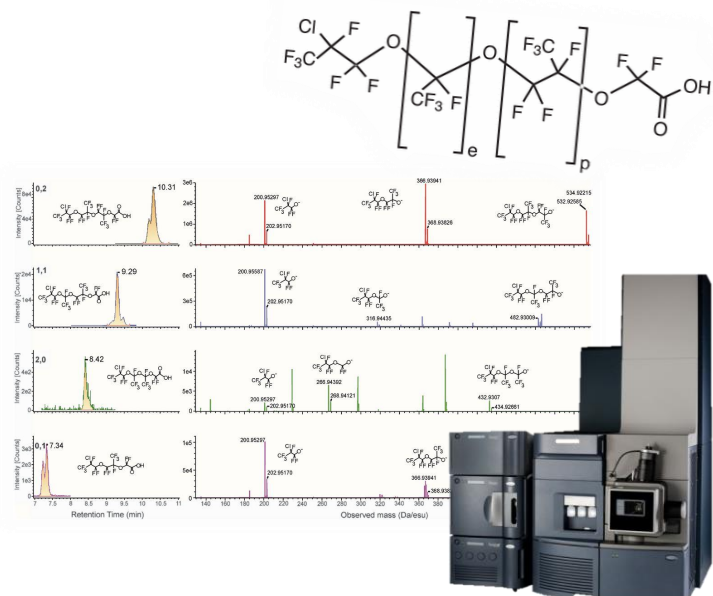


Semi-quantitation of compounds for environmental source analysis

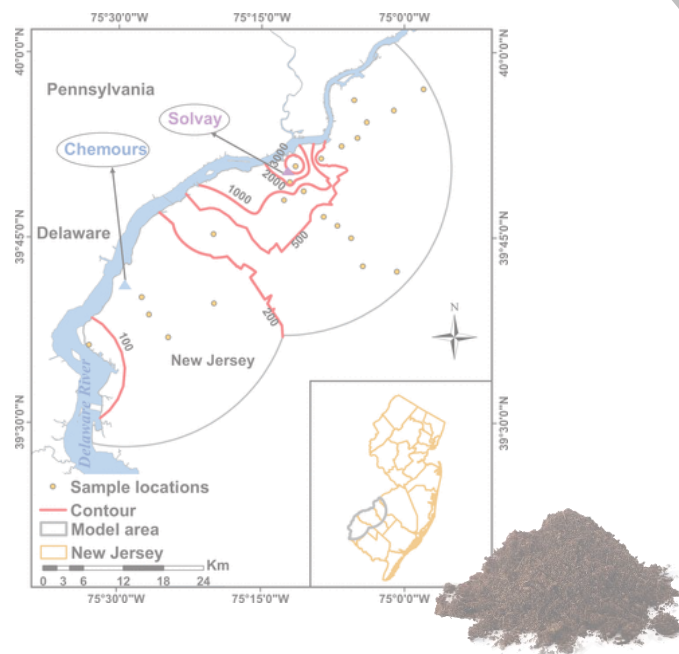


Partitioning of next-generation PFAS compounds in vegetation and soil cores

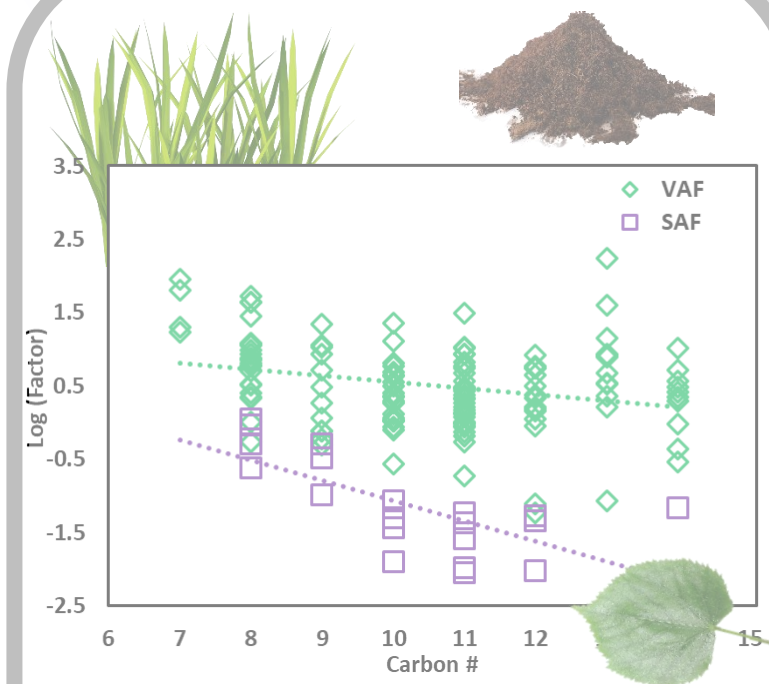




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# Sample Prep: Surface Soil Extraction

## Extraction

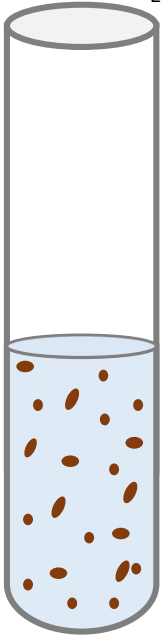


Surface soil sample  
Dried, sieved

# Sample Prep: Surface Soil Extraction

## Extraction

$^{13}\text{C}_8\text{-PFOA}$   
NaOH  
90:10 ACN/ $\text{H}_2\text{O}$

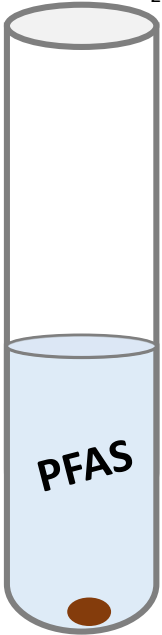


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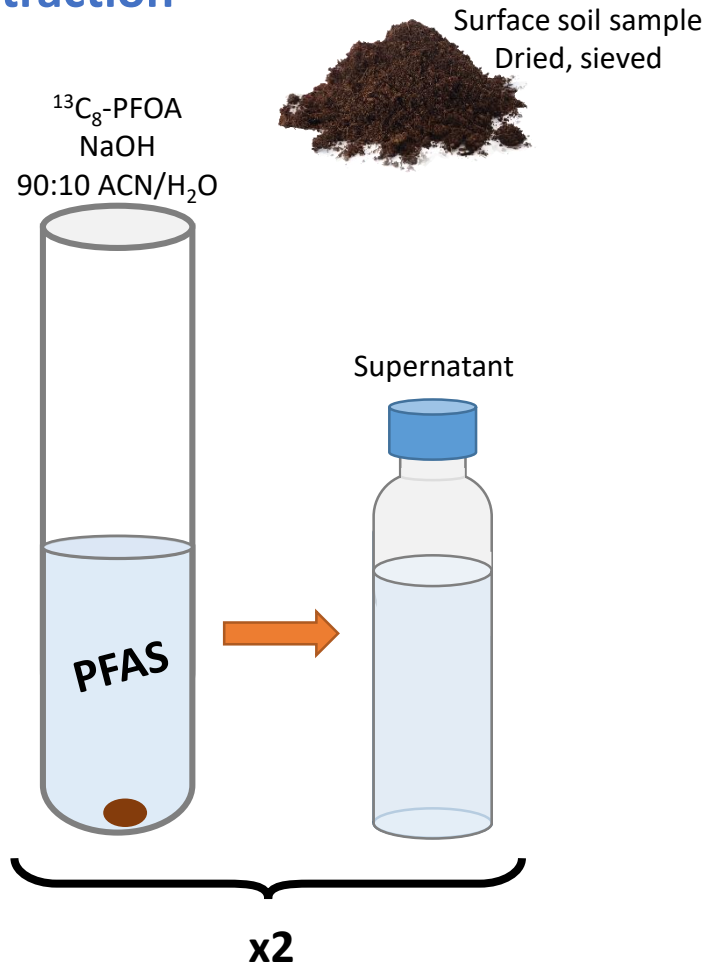
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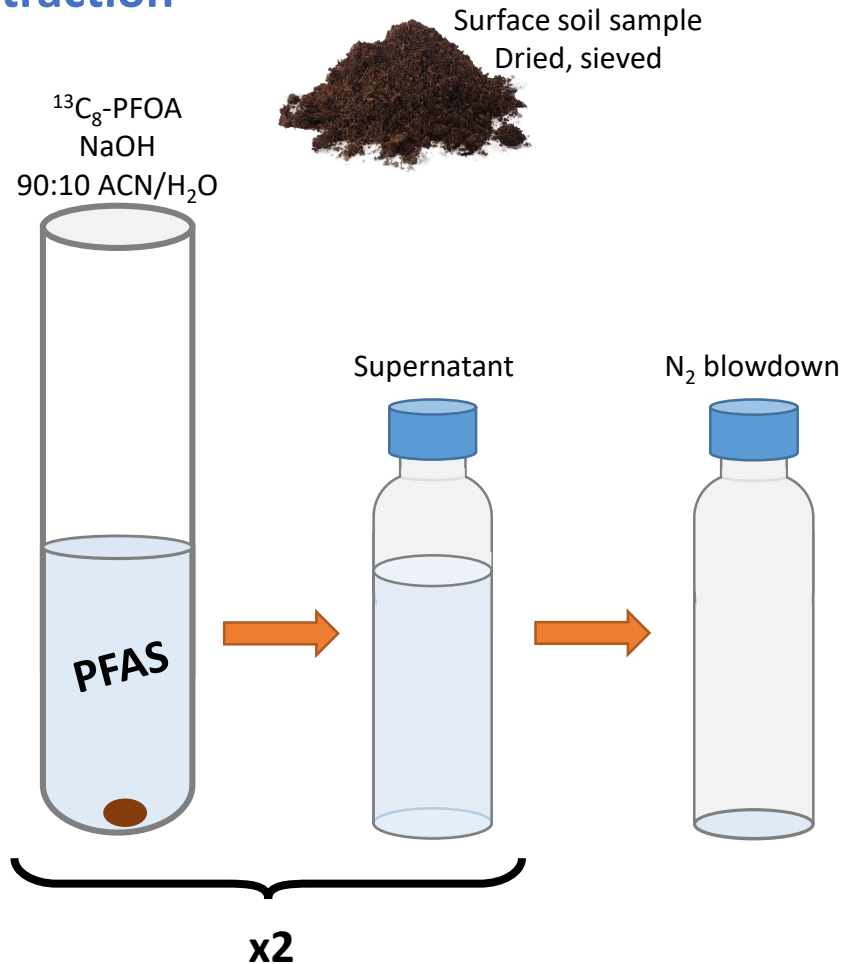
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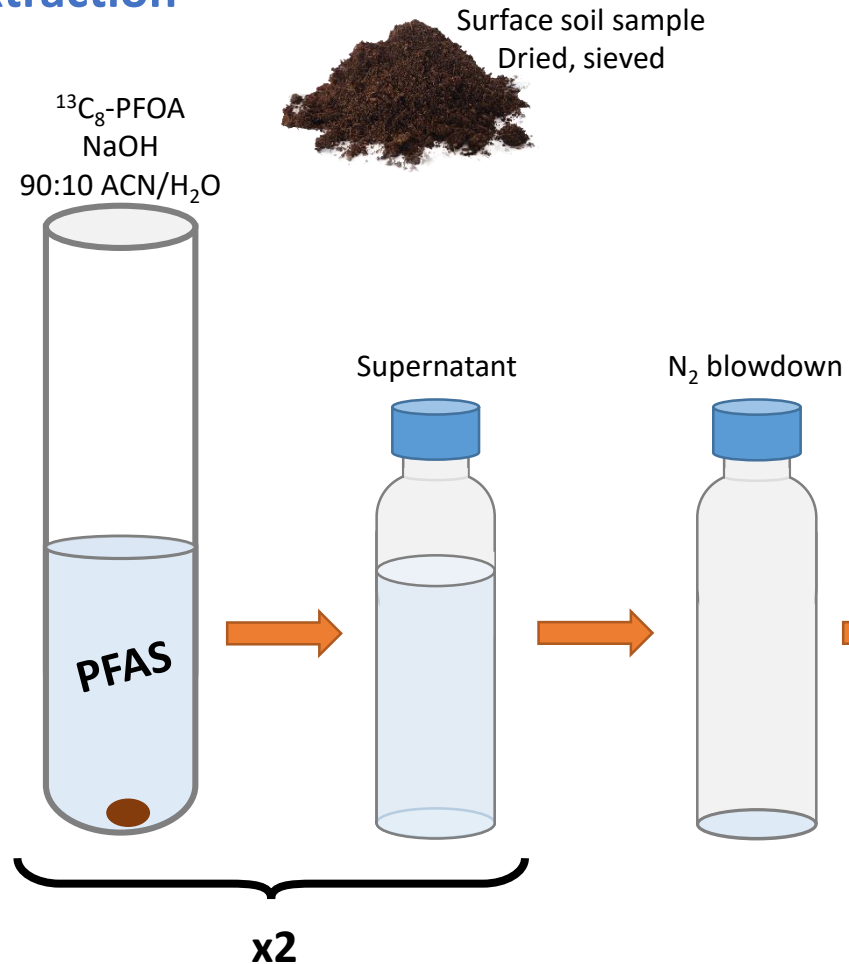
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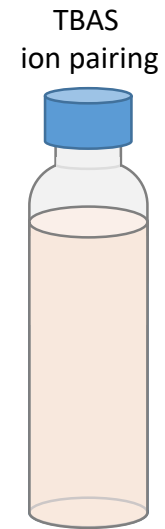


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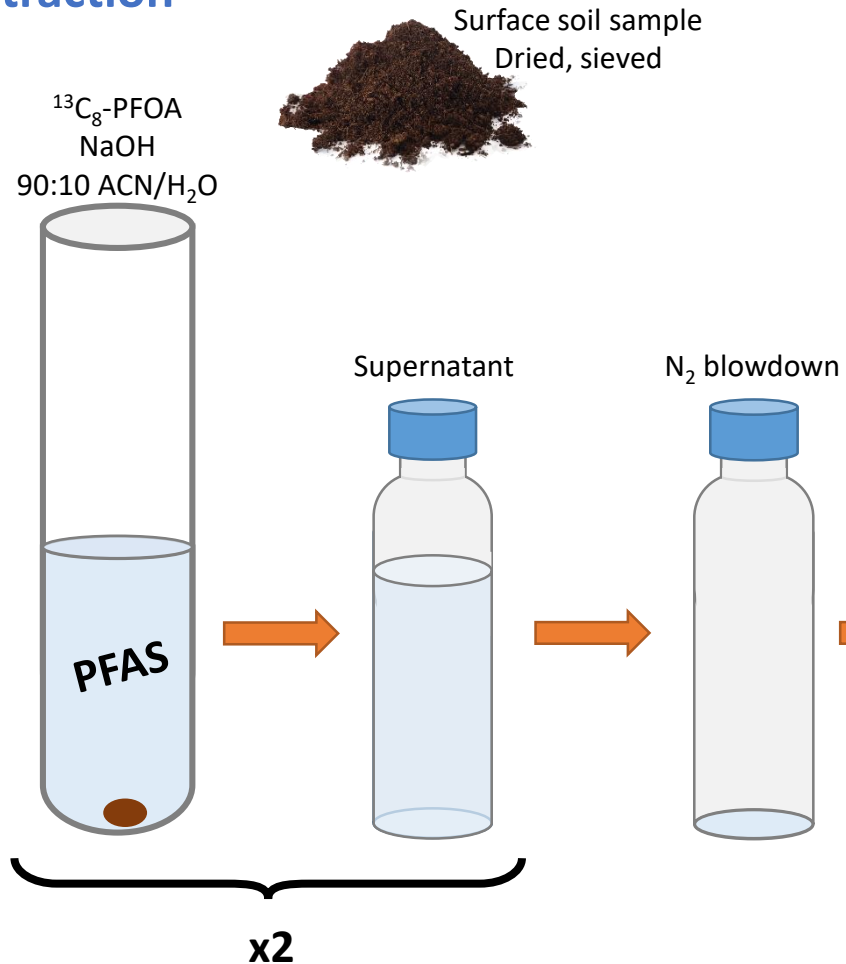
## Clean up



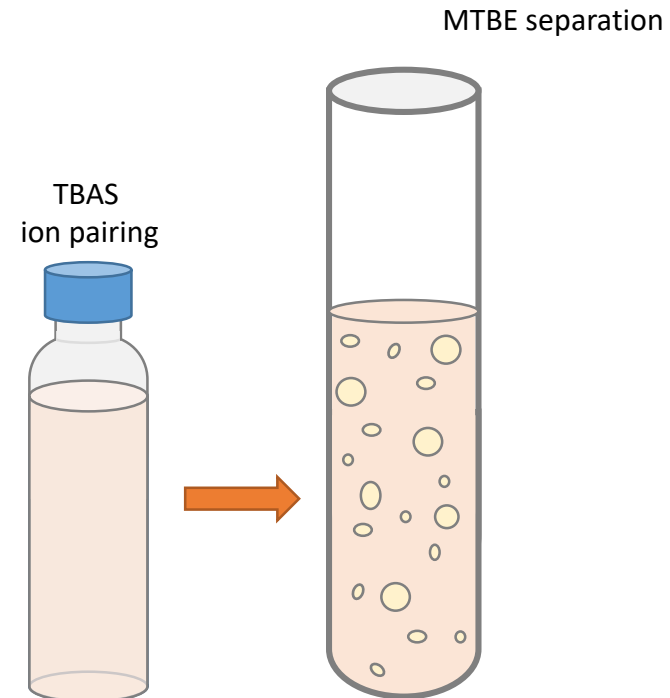


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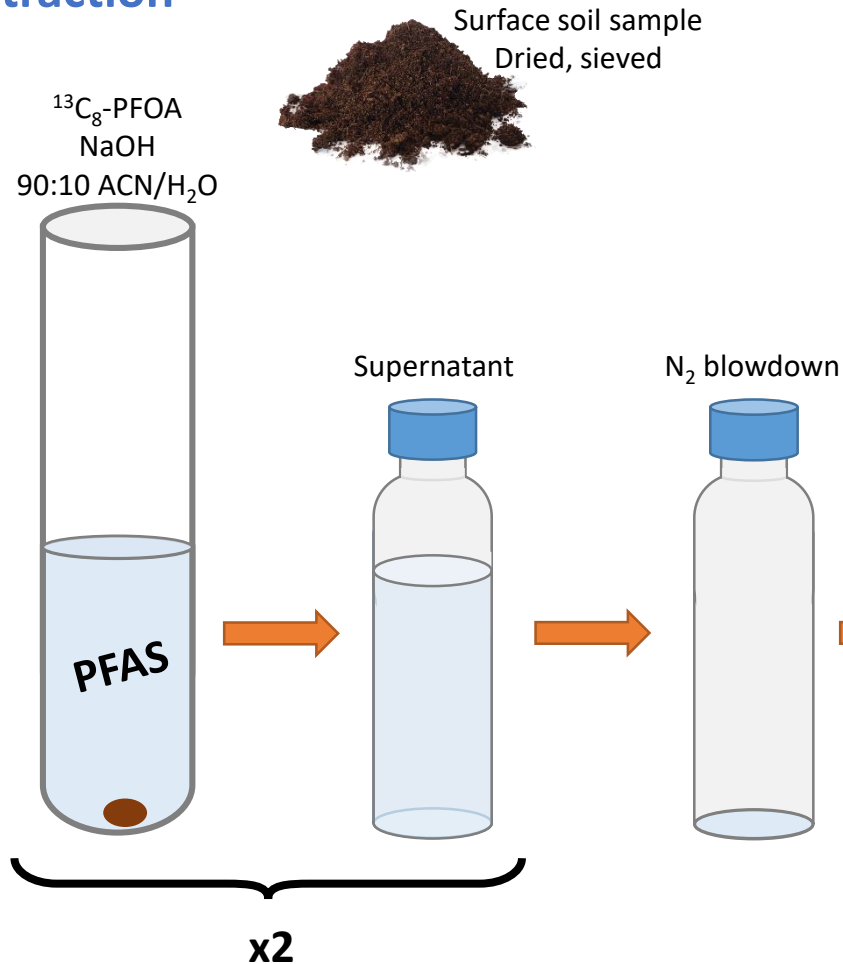


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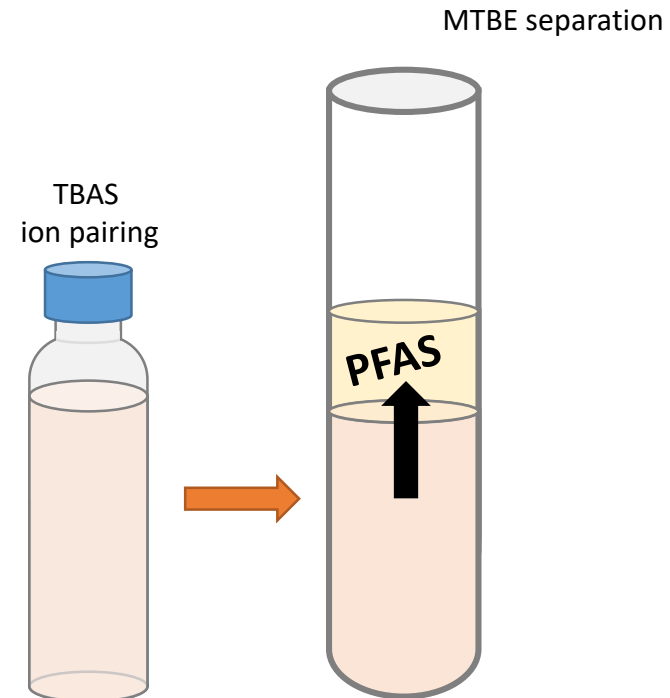


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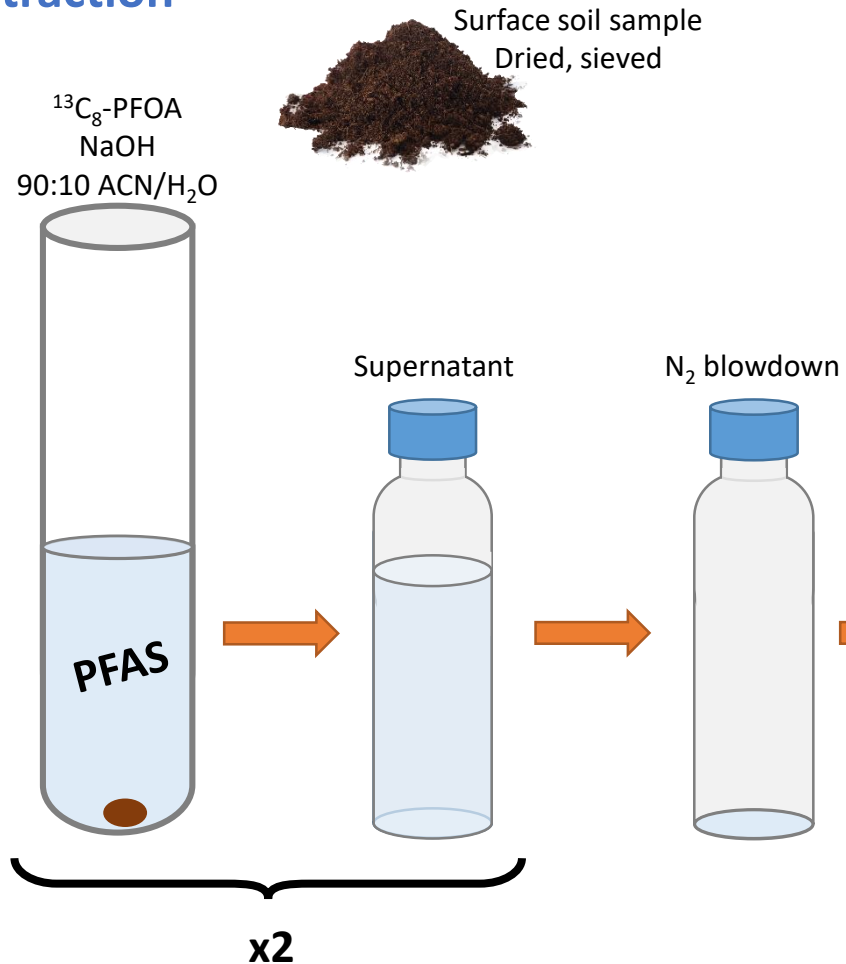


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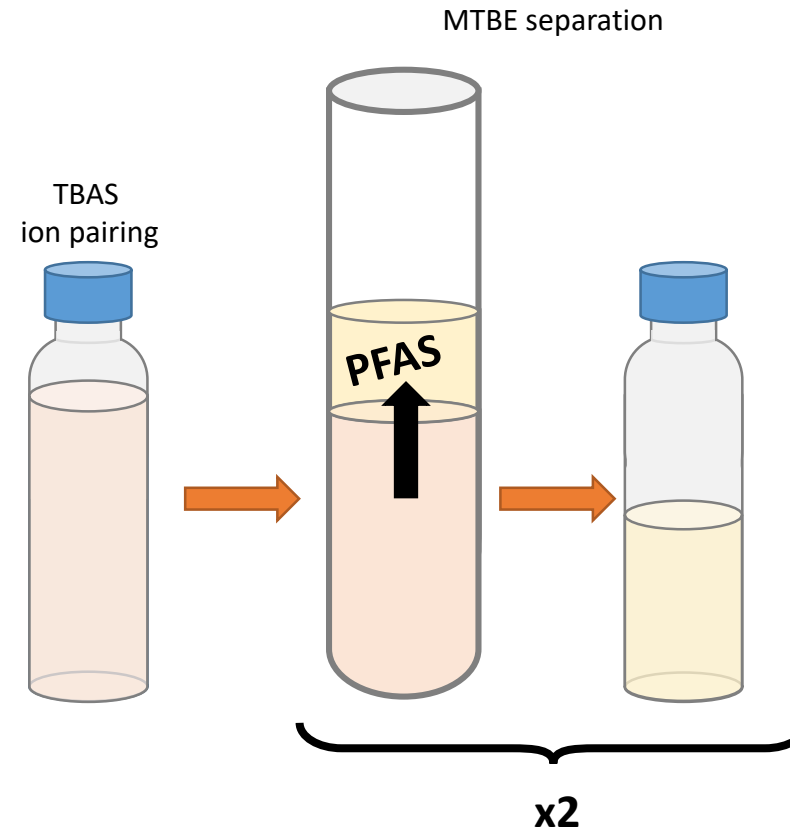


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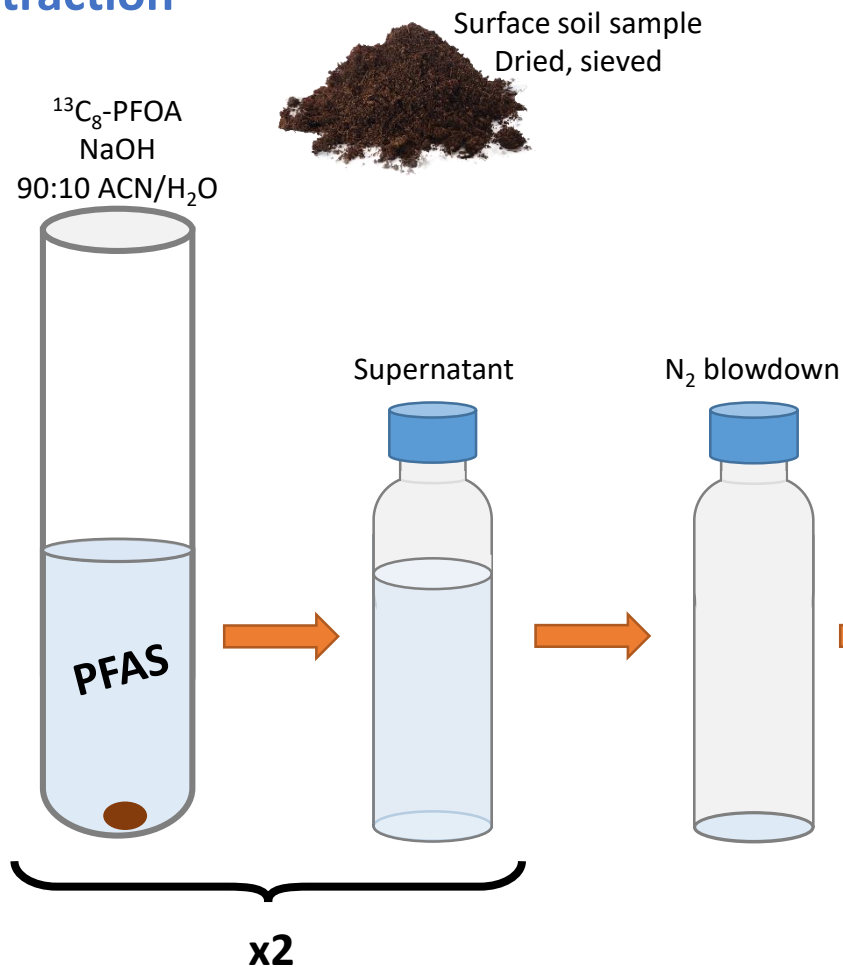


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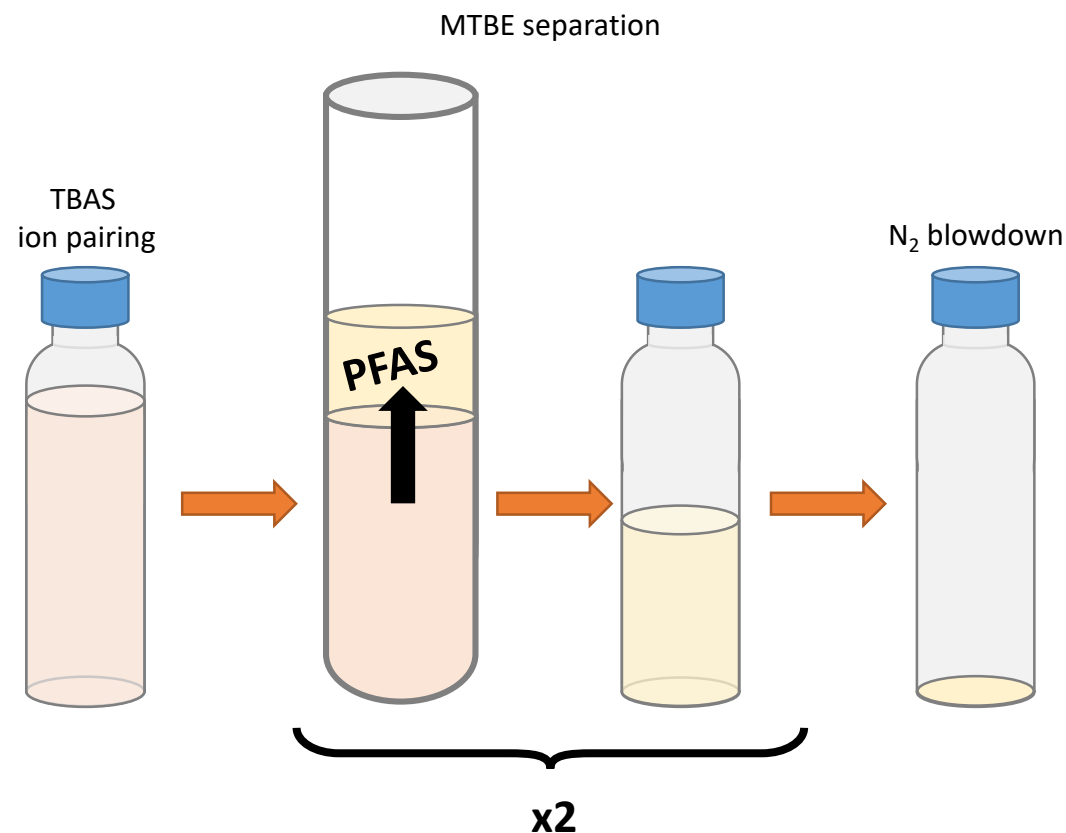


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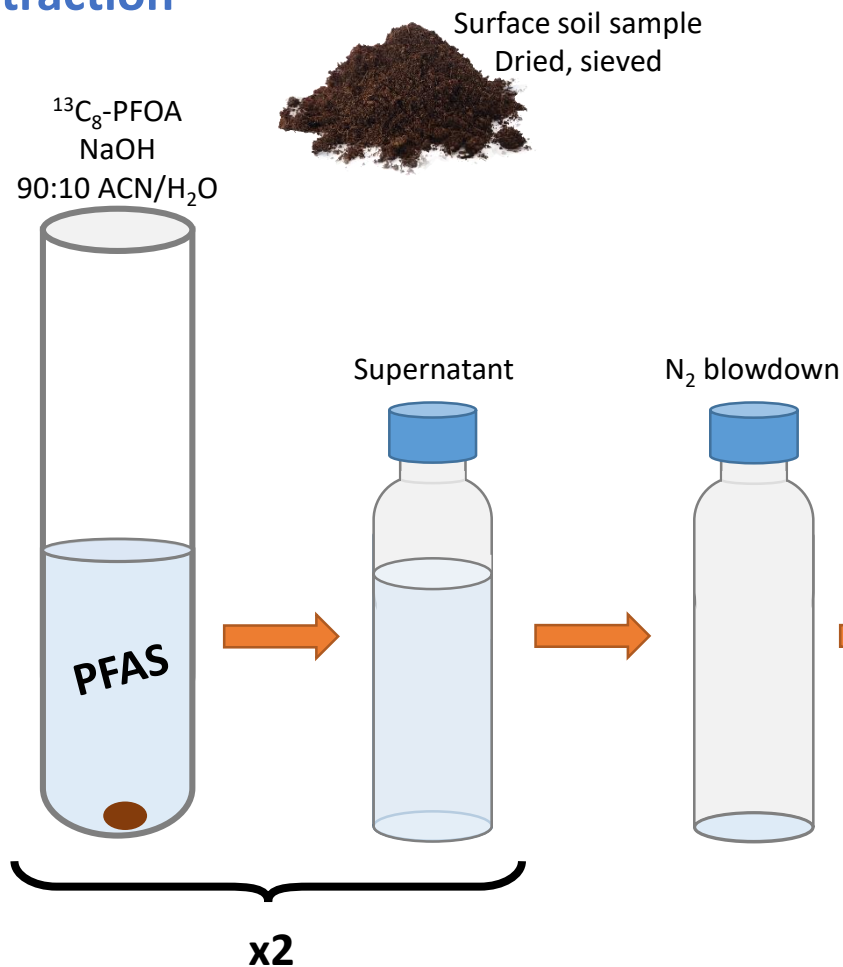


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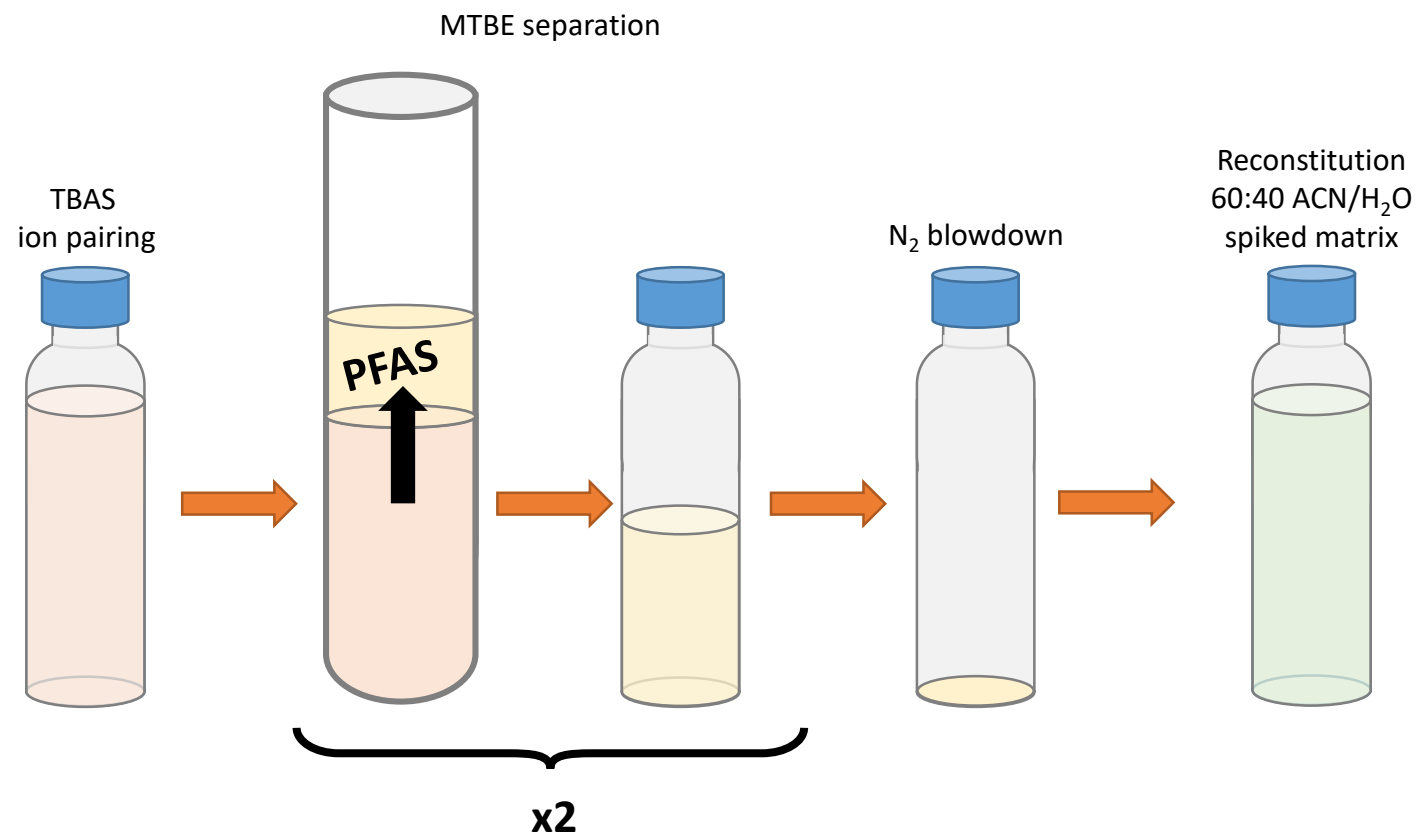


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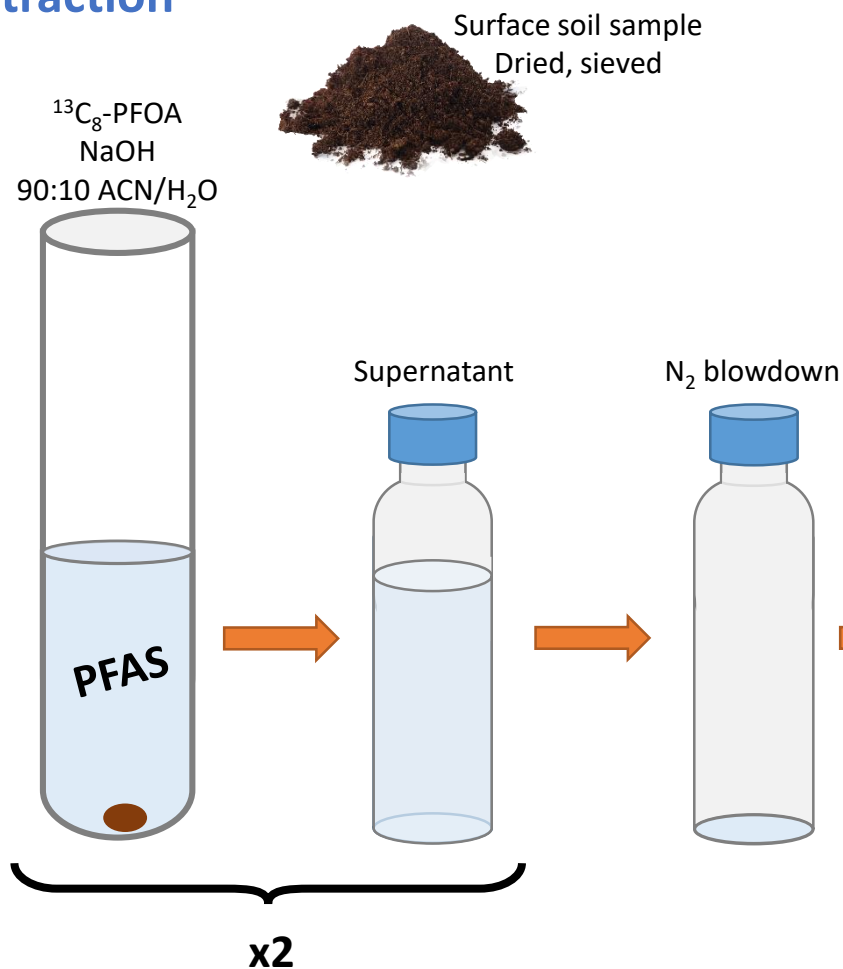


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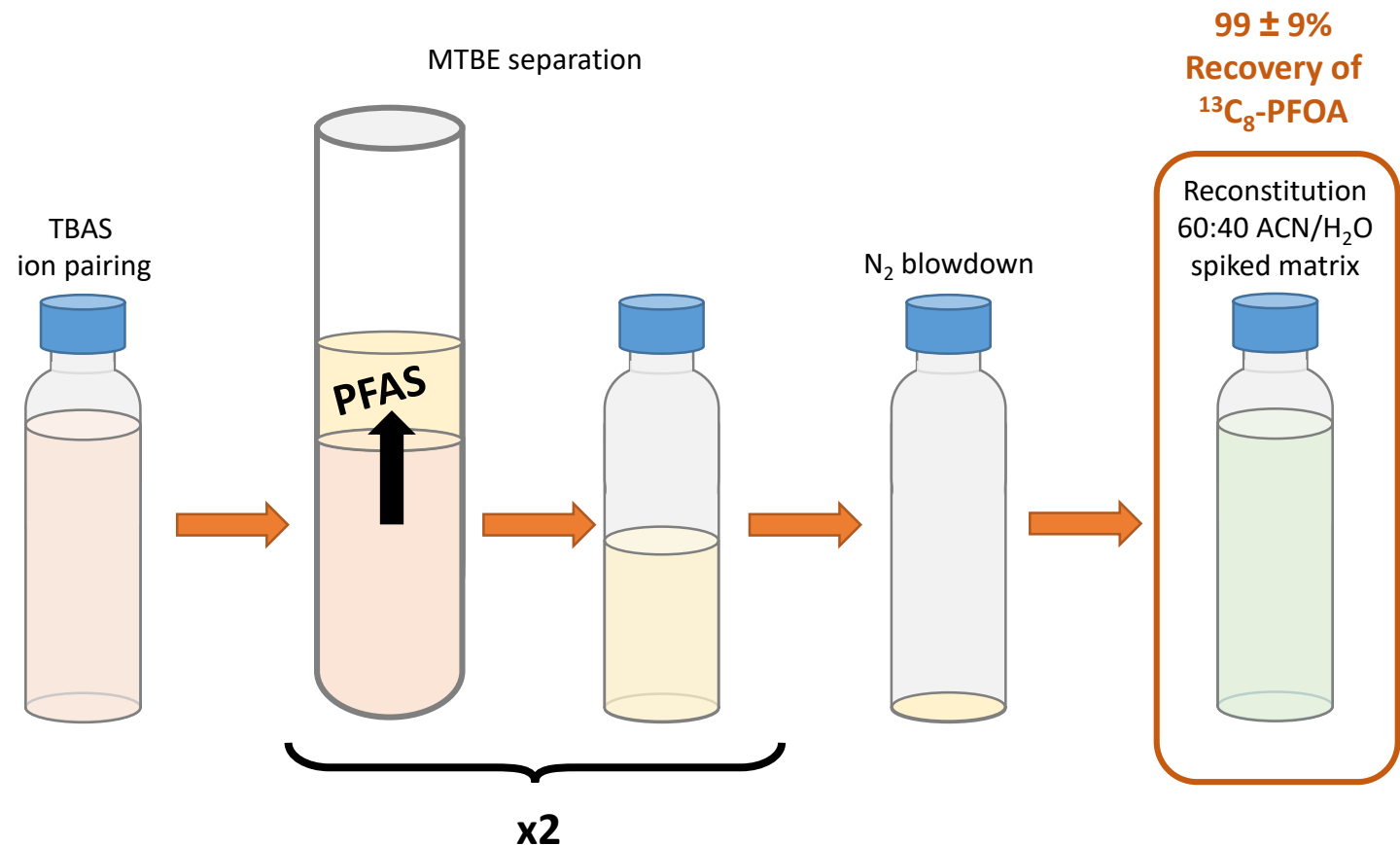


# Sample Prep: Surface Soil Extraction

## Extraction



## Clean up





- Waters Acquity UPLC coupled to a Waters Xevo G2-XS QToF
  - Negative electrospray ionization (ESI)
  - Acquity BEH C18 column
  - Leucine enkephalin lock mass reference injected every 30 sec during run

UPLC	QToF
<ul style="list-style-type: none"> <li>• 0.15 mL/min flow rate</li> <li>• Linear gradient 20:80 to 90:10 ACN/H<sub>2</sub>O over 20 min</li> </ul>	<ul style="list-style-type: none"> <li>• MS<sup>e</sup> and MS/MS mode</li> <li>• Collision energy ramped 11-25 V</li> </ul>



Library  
Search

## Data Reduction

- High signal intensity (top 1000)
- Mass defect ranging from -0.10 to +0.05 Da
- Appearance in multiple samples

## Evaluation of Molecular Formula

- Exact mass
- Carbon number
- High and low collision energy spectra
- Spectral features

Literature  
Search

Library Search

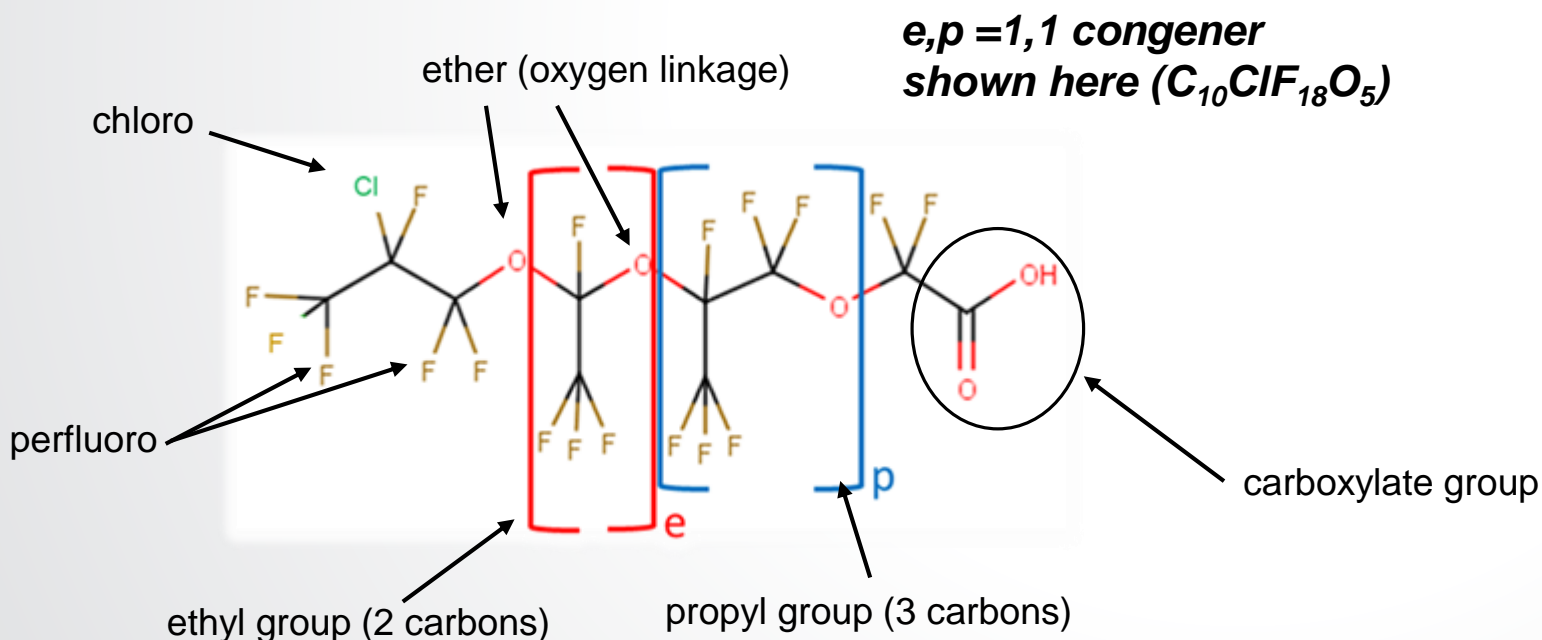
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Chloroperfluoropolyether carboxylates (CIPFPECAs)

- Congeners designated by ethyl,propyl (e,p) count

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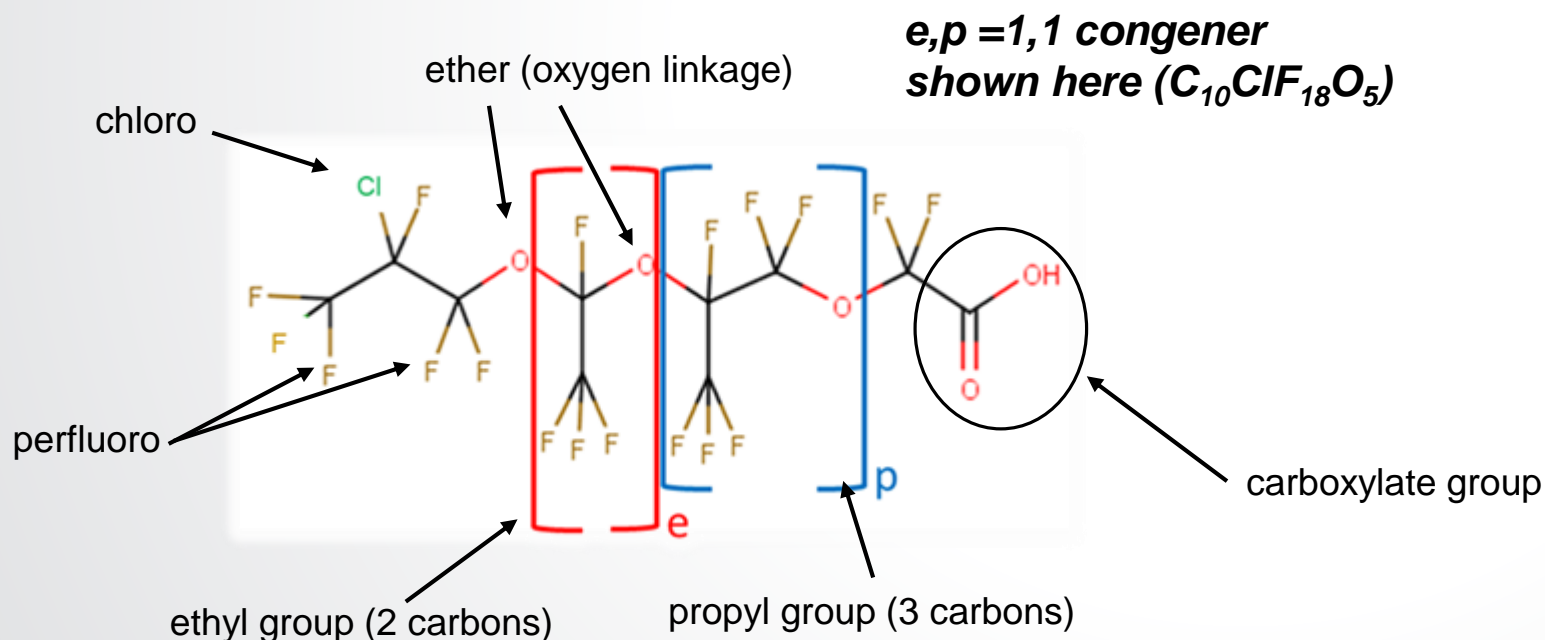
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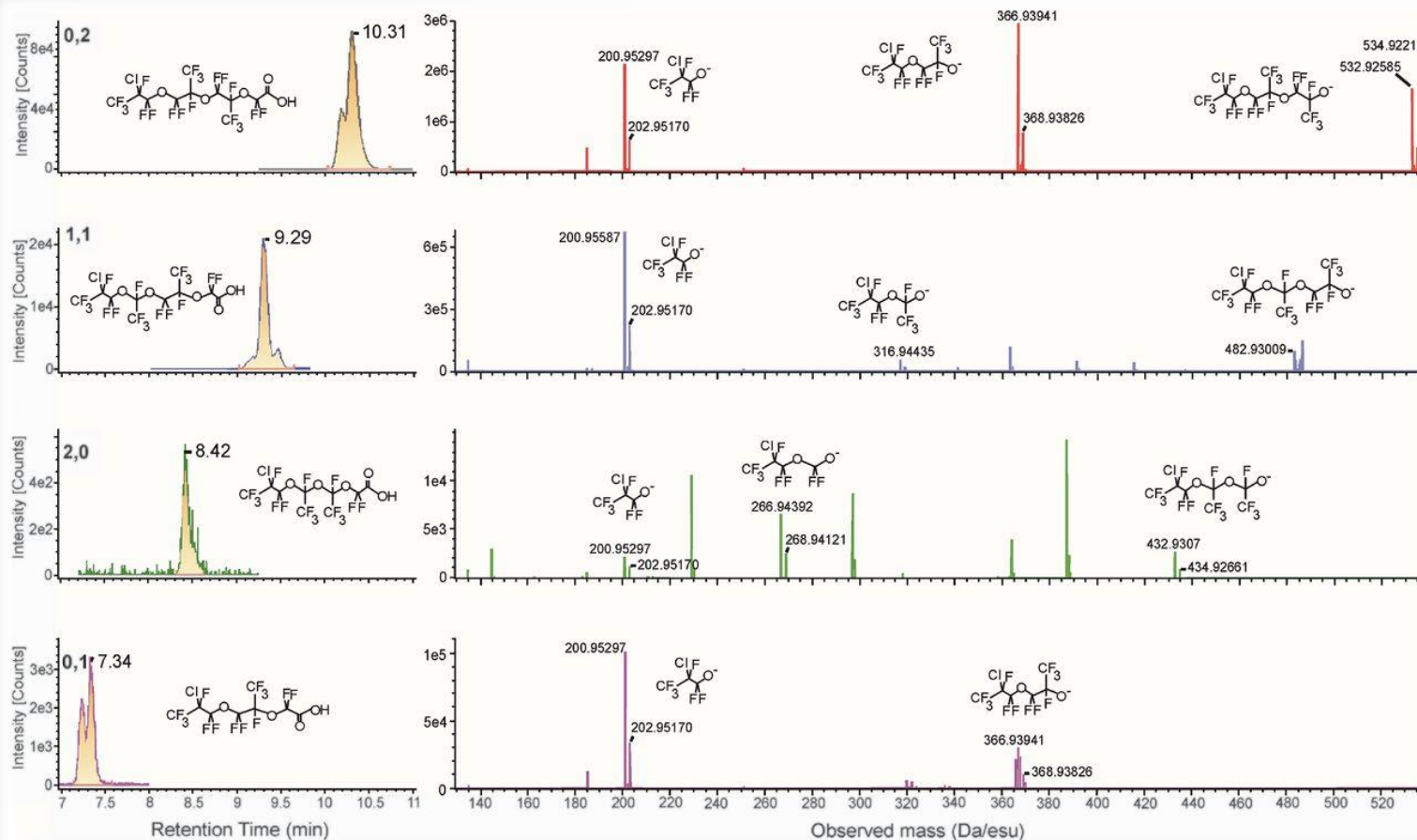
Chloroperfluoropolyether  
carboxylates (CIPFPECAs)

- Congeners designated by ethyl,propyl (e,p) count

Suspect  
Screening

Further  
Elucidation  
MS/MS mode

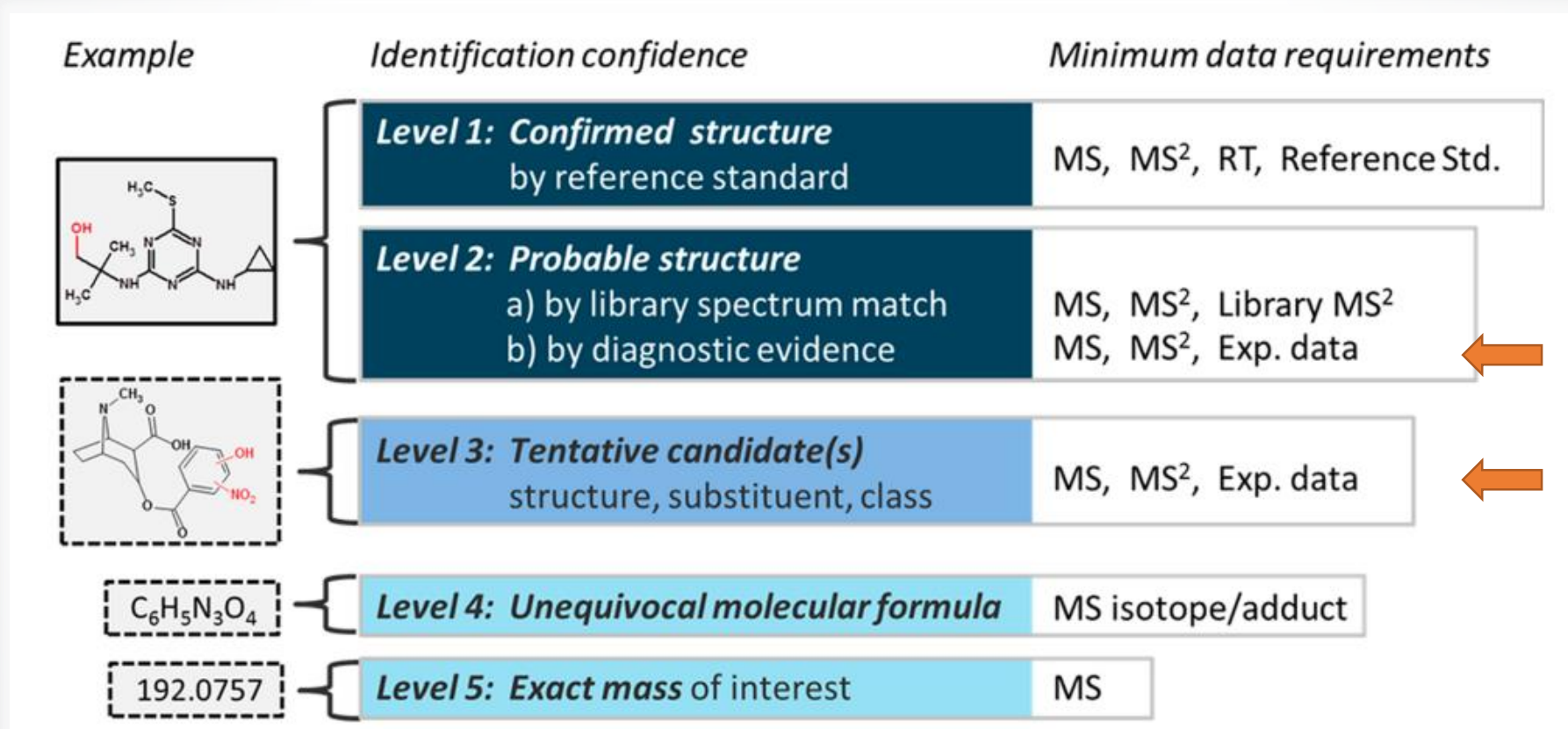
# Structural Elucidation: MS/MS Mode



- Focused quadrupole on precursor masses
- Fragmented with ramped collision energy
- Isolated fragments in ToF
- Fragmentation patterns supported structural elucidation
- Common fragments furthered suspect screening efforts

# Tentative Identification

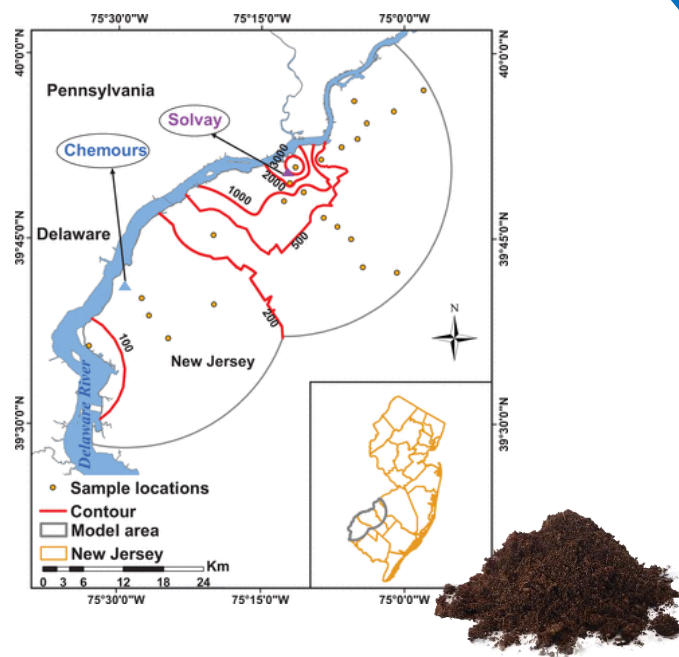
## 9 Congeners tentatively identified in NJ surface soils



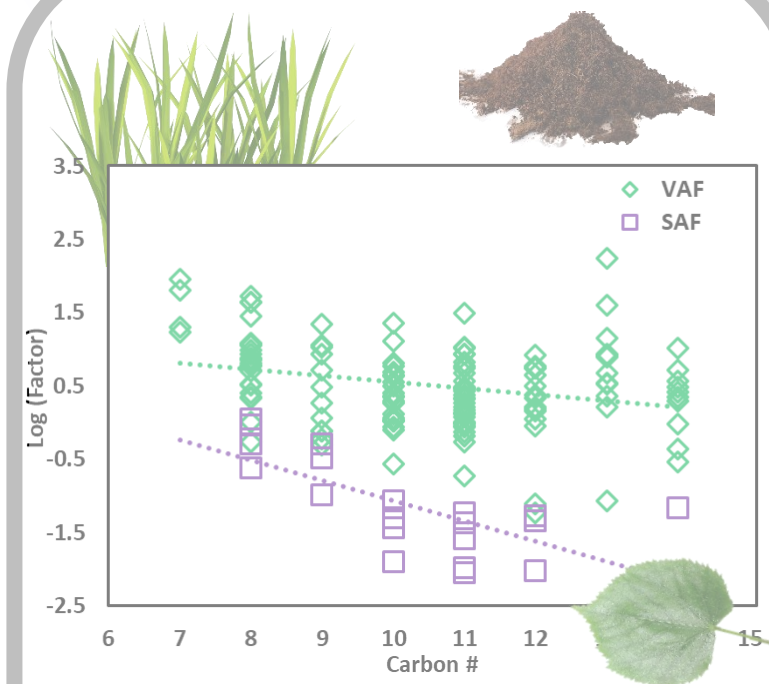




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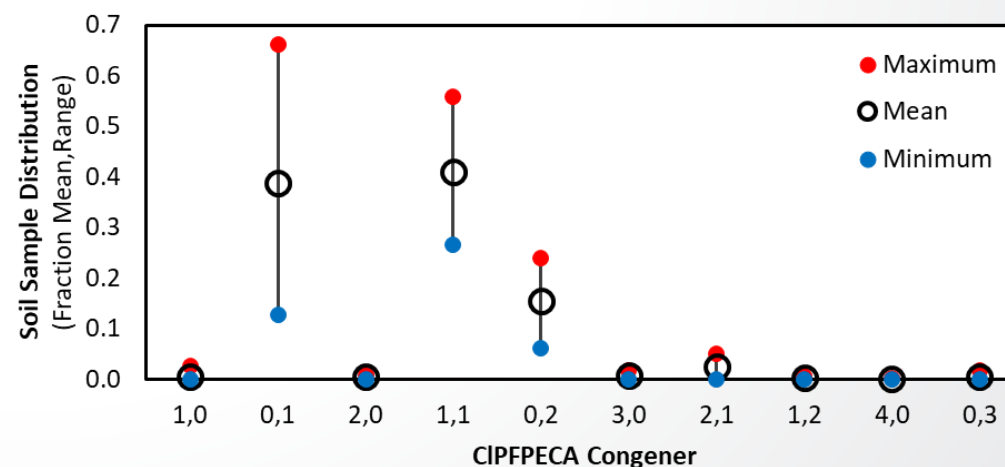
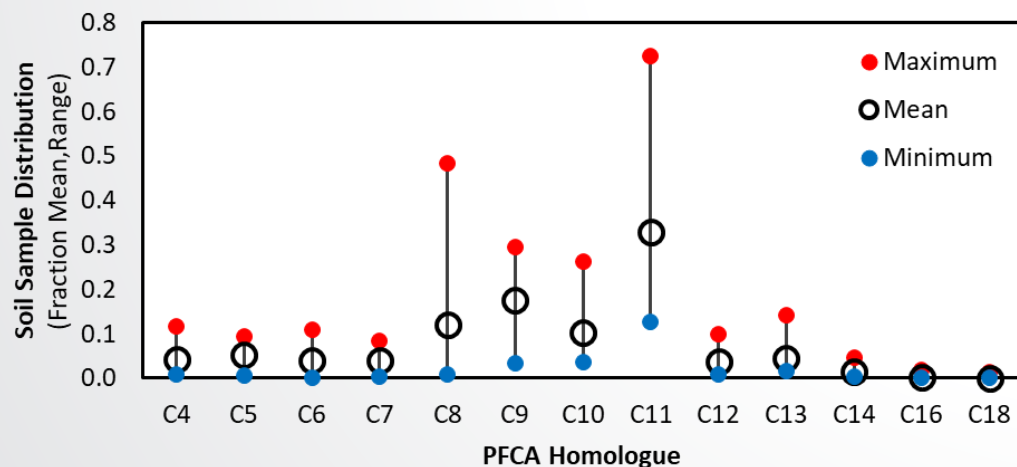


Semi-quantitation of compounds for environmental source analysis



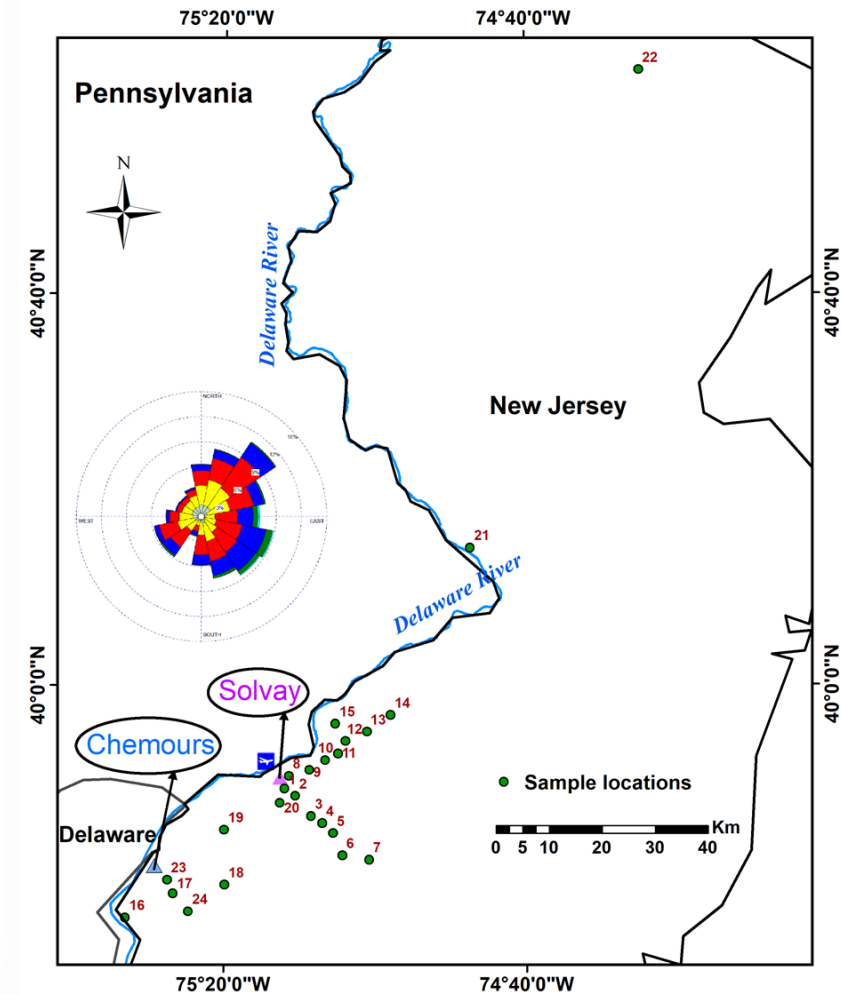
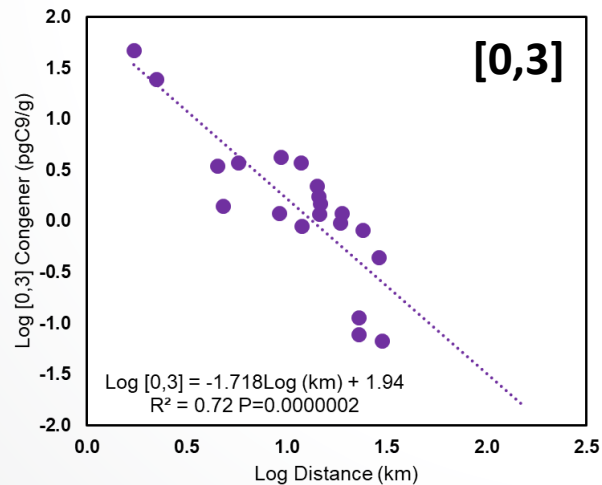
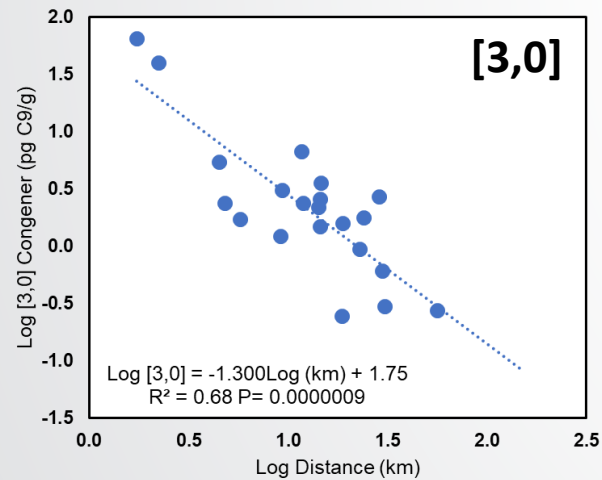
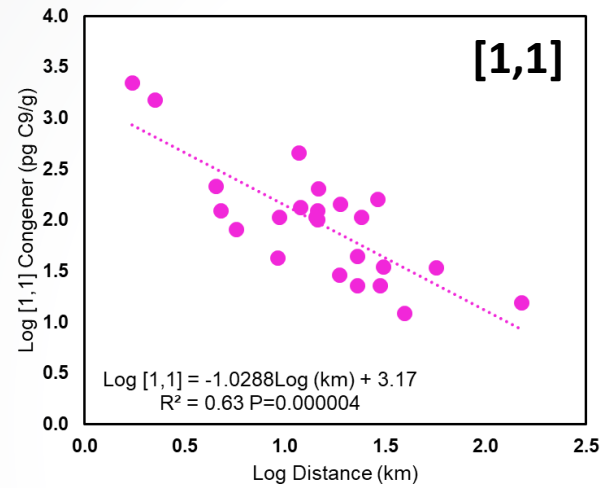
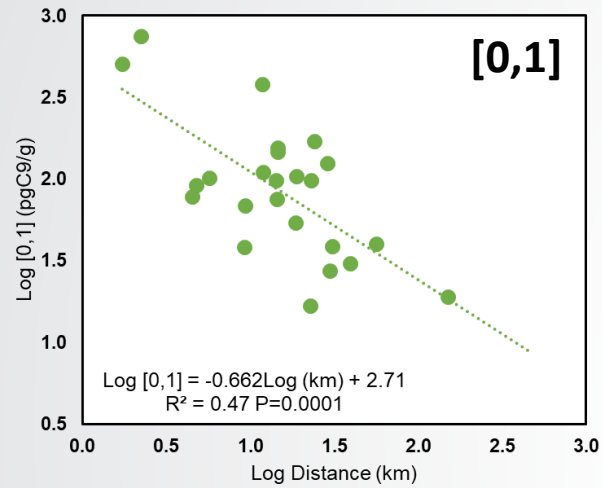
Partitioning of next-generation PFAS compounds in vegetation and soil cores

- Data from high resolution mass spectroscopy (HRMS) informed development of transitions in MRM methods for conventional-resolution LC-MS/MS
  - Waters Acquity UPLC coupled to a Waters Quattro Premier triple-quadrupole mass spectrometer
- Normalized peak intensities of ClPFECAs by  $^{13}\text{C}_5$ -PFNA internal standard and expressed “concentrations” as C9 (PFNA)



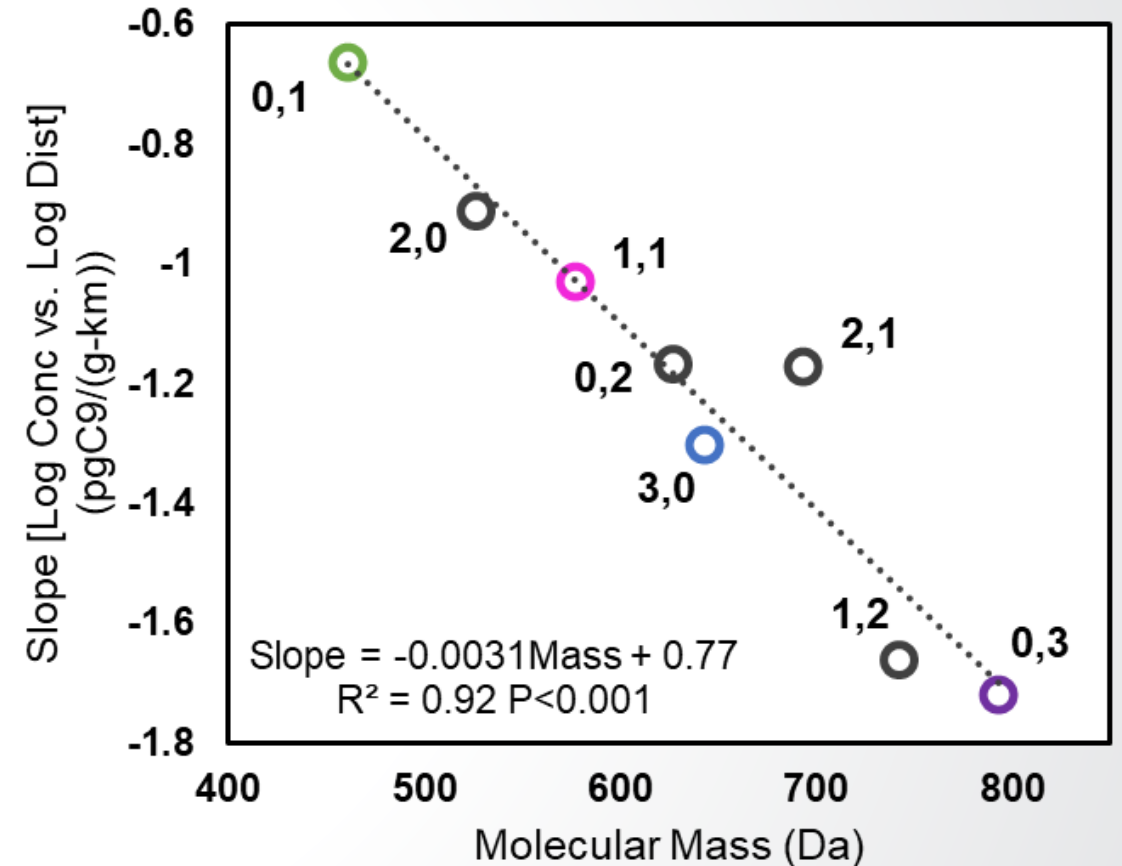
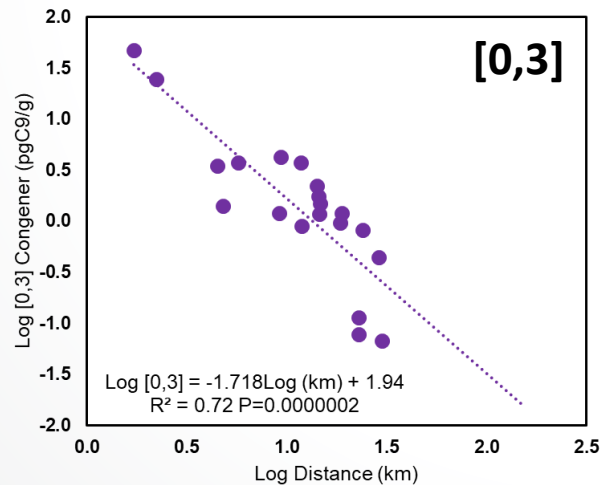
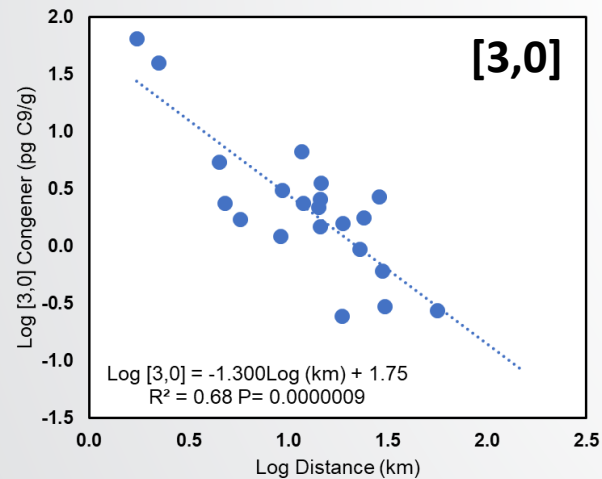
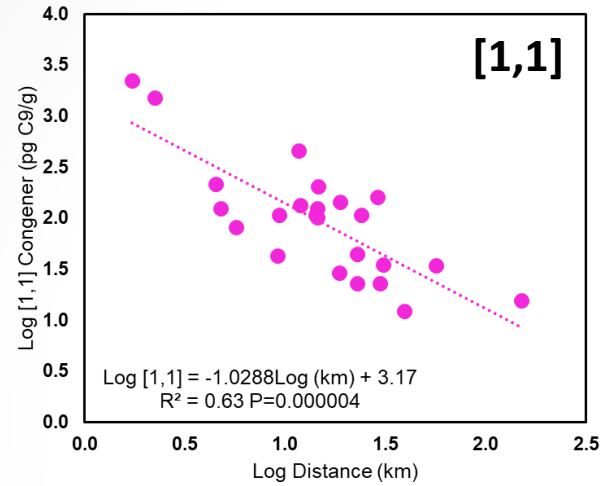
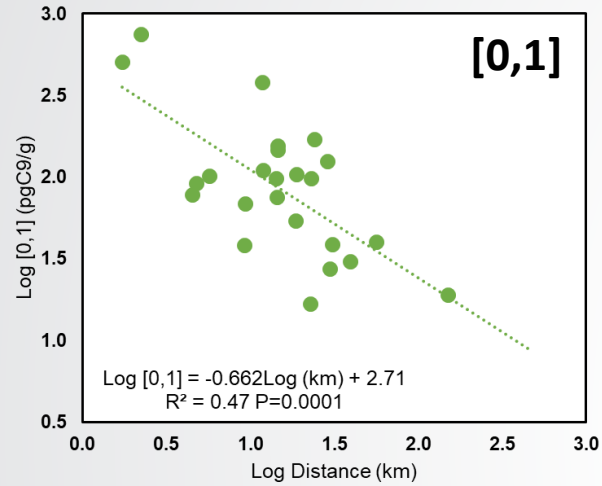


# Compound Mass-Dependent Deposition





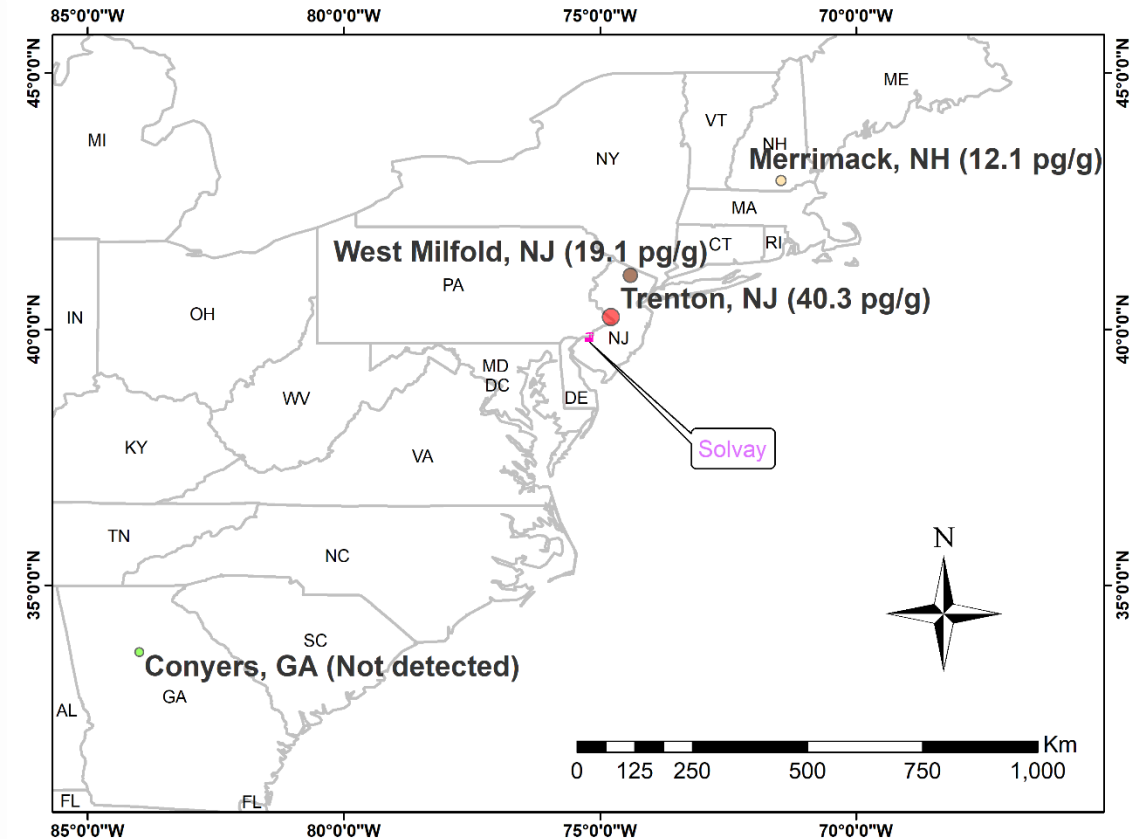
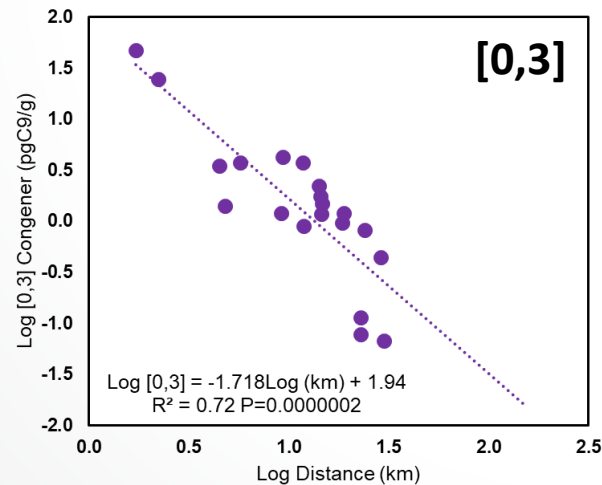
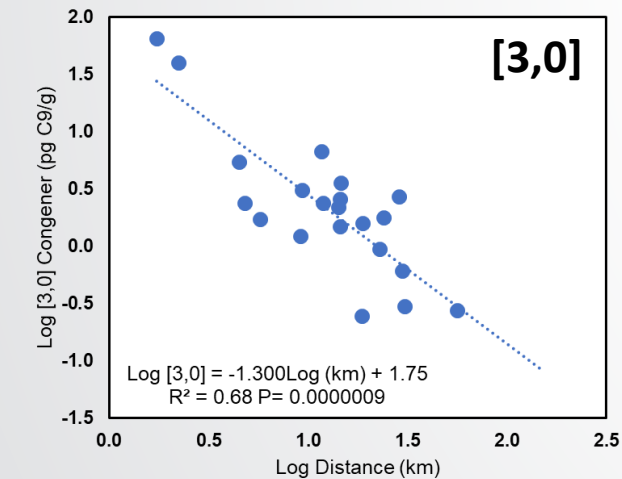
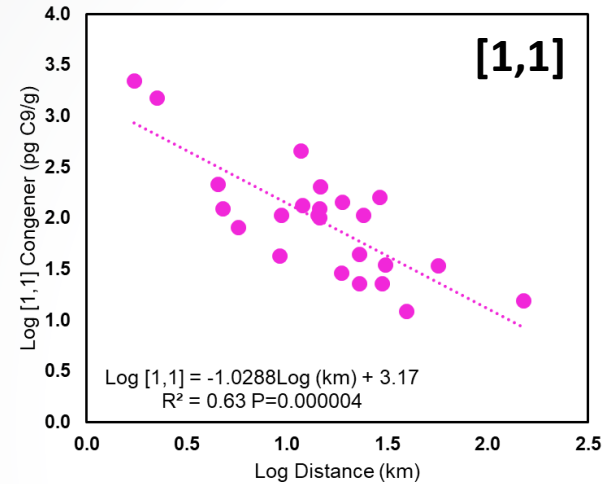
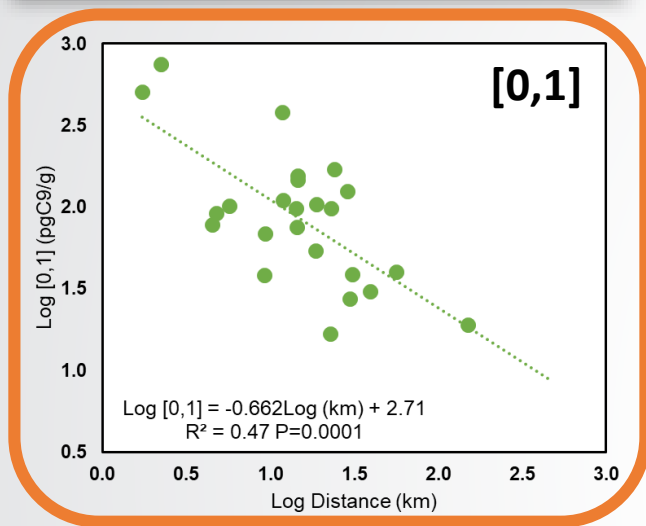
# Compound Mass-Dependent Deposition



- Lower slope indicates faster drop off in concentration
- Congeners with lower mass have slower drop off in concentration, indicating wider dispersion

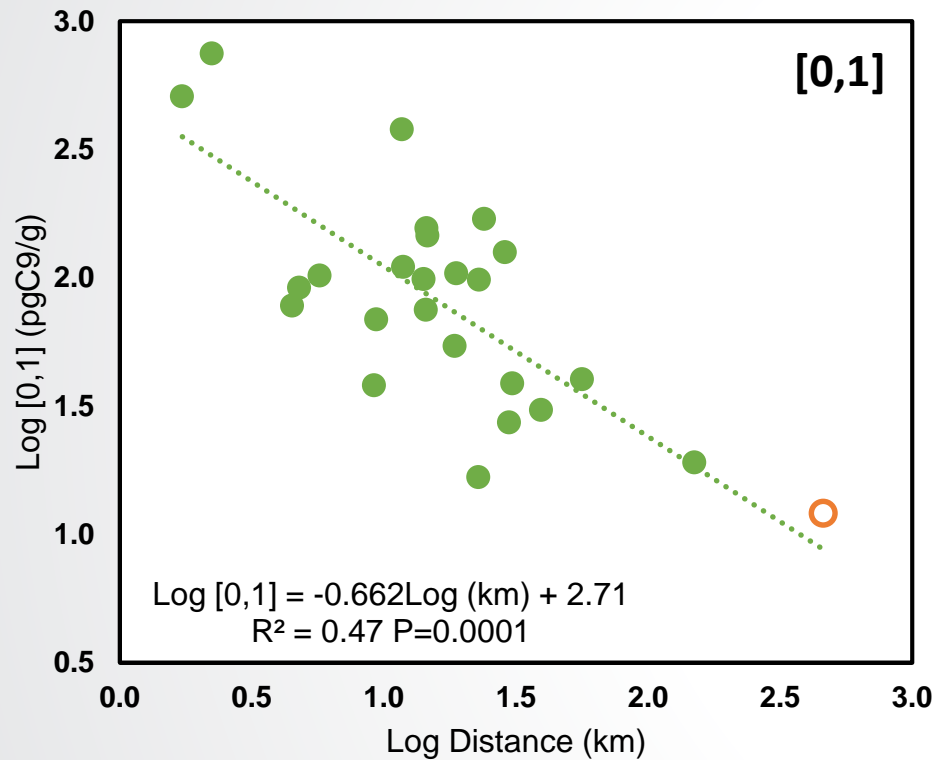


# Compound Mass-Dependent Deposition

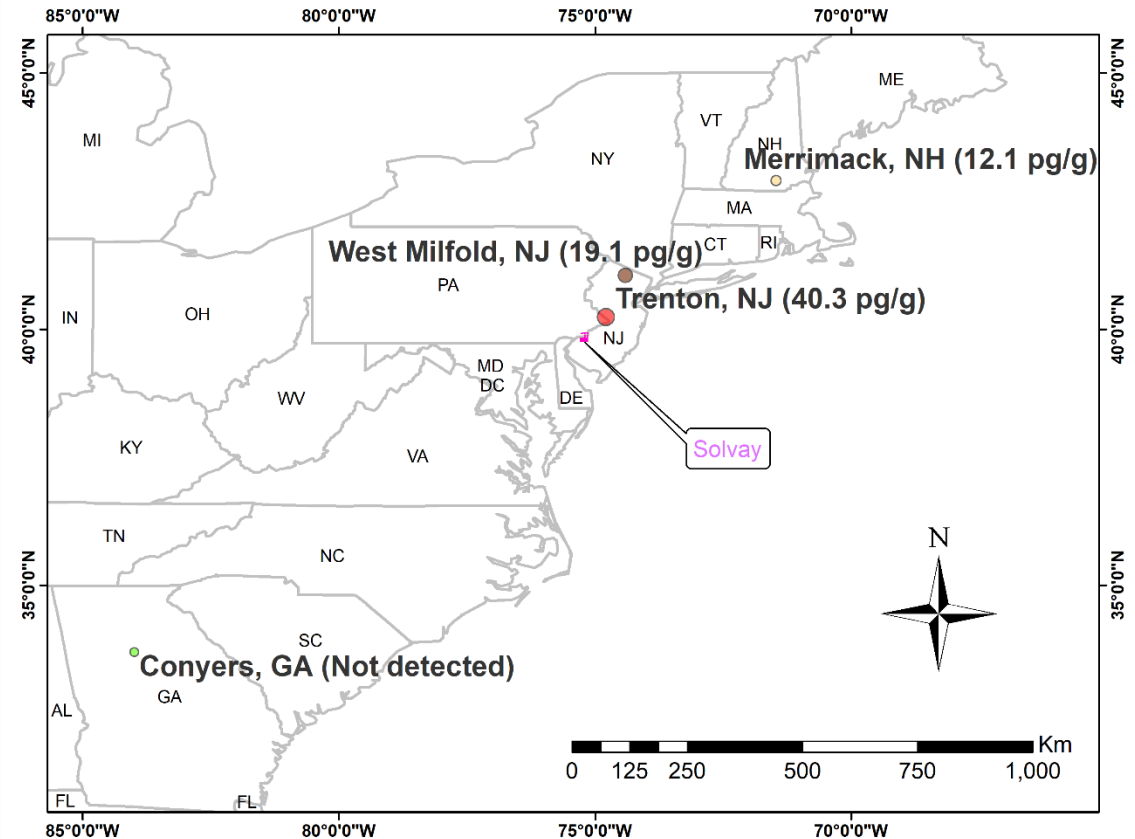


- Independently collected sample from New Hampshire lies roughly along transect

# Compound Mass-Dependent Deposition



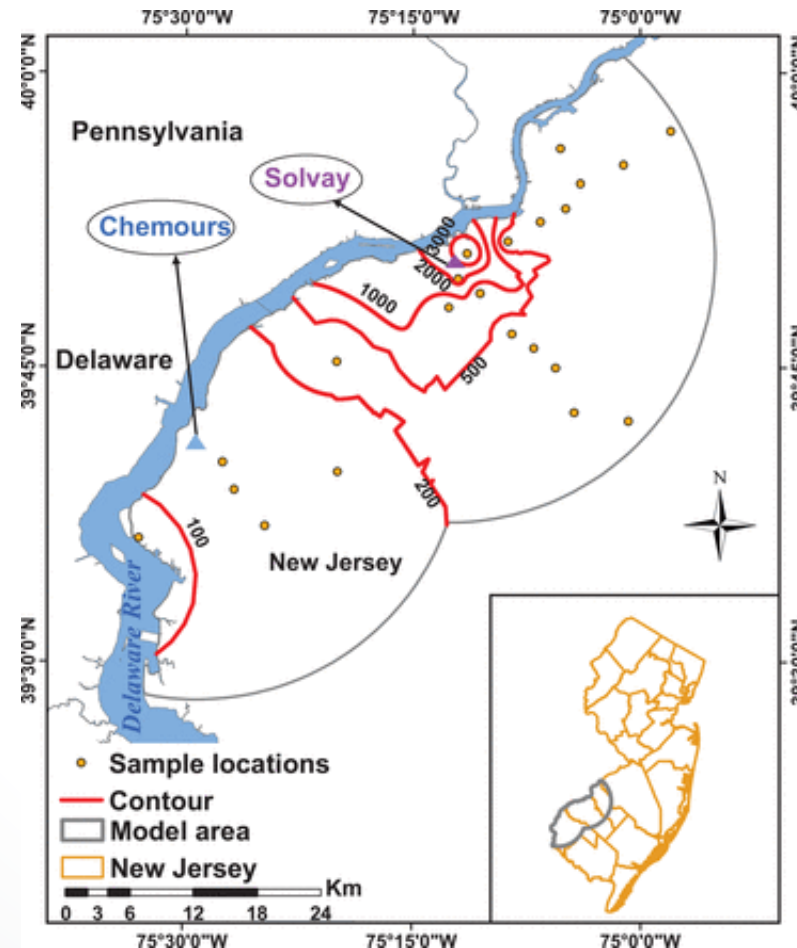
- For [0,1] congener (lowest mass), NH sample concentration lies along trend line



- Independently collected sample from New Hampshire lies roughly along transect



# Concentration Contours Suggest Industrial Source

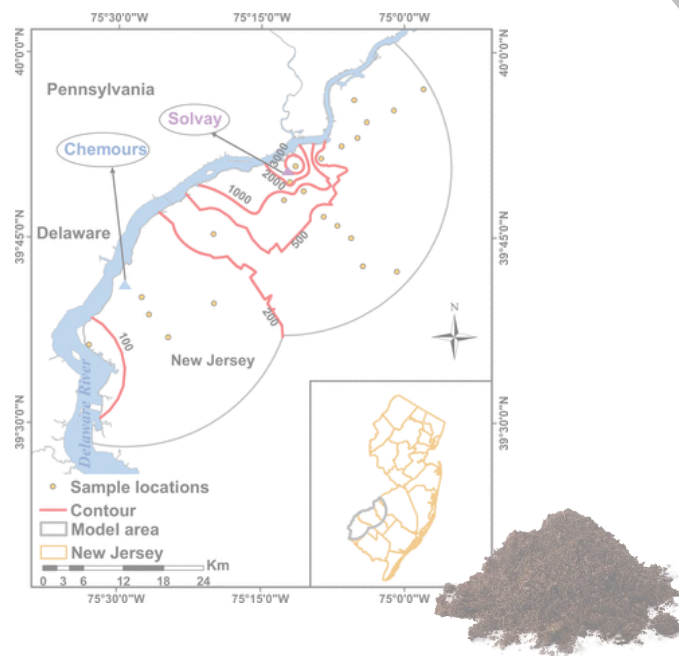


Washington et al. *Science*, **368**, 1103-1107 (2020).

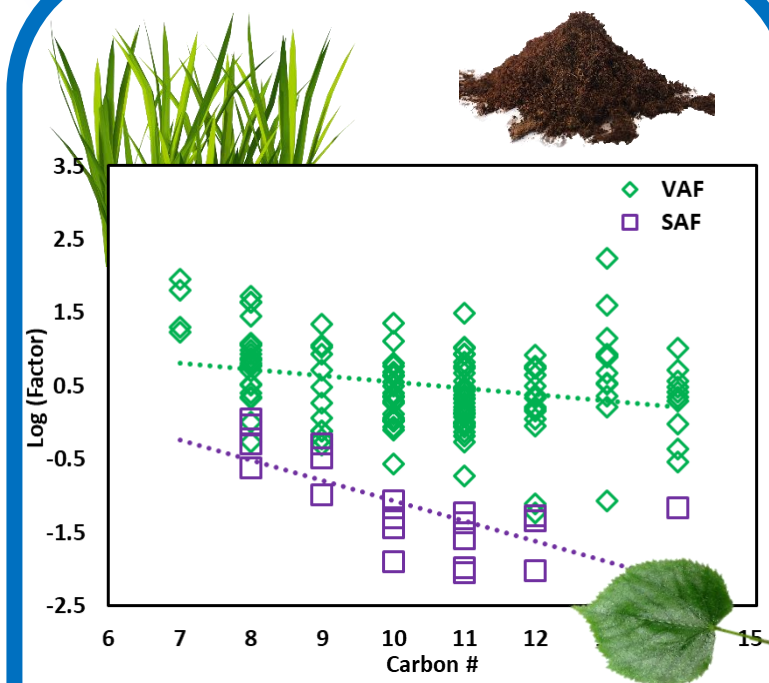




Method for detecting the presence of next-generation PFAS in NJ environmental samples via nontargeted analysis



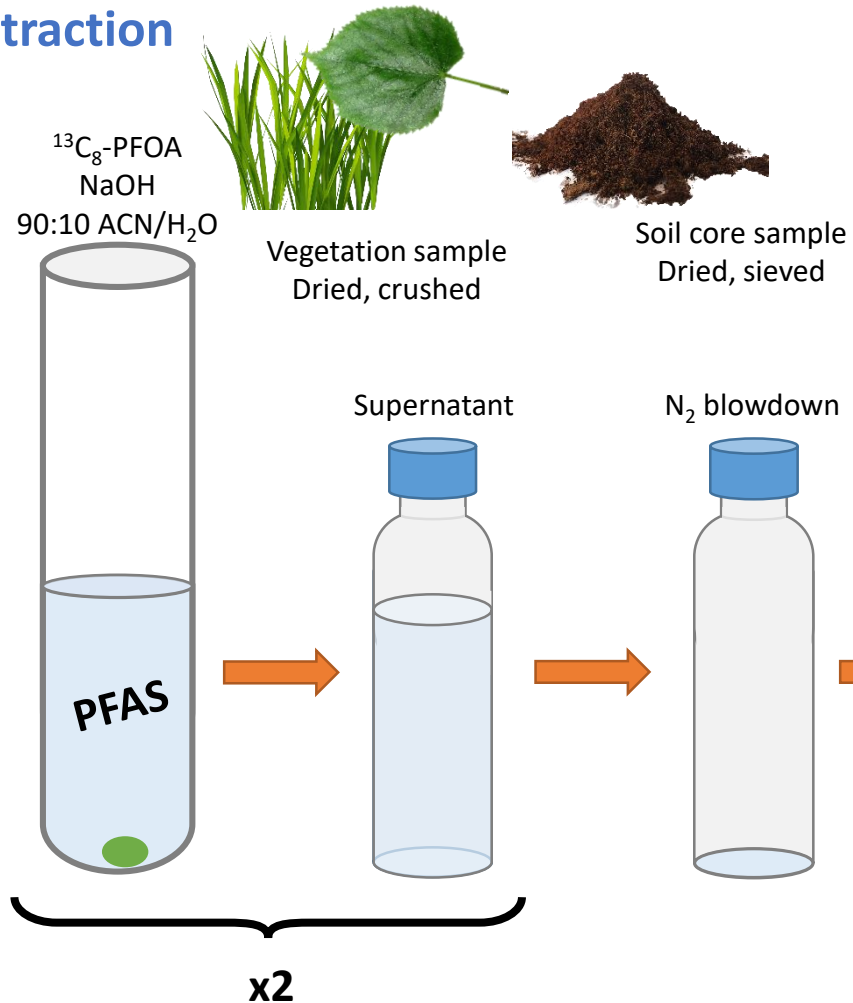
Semi-quantitation of compounds for environmental source analysis



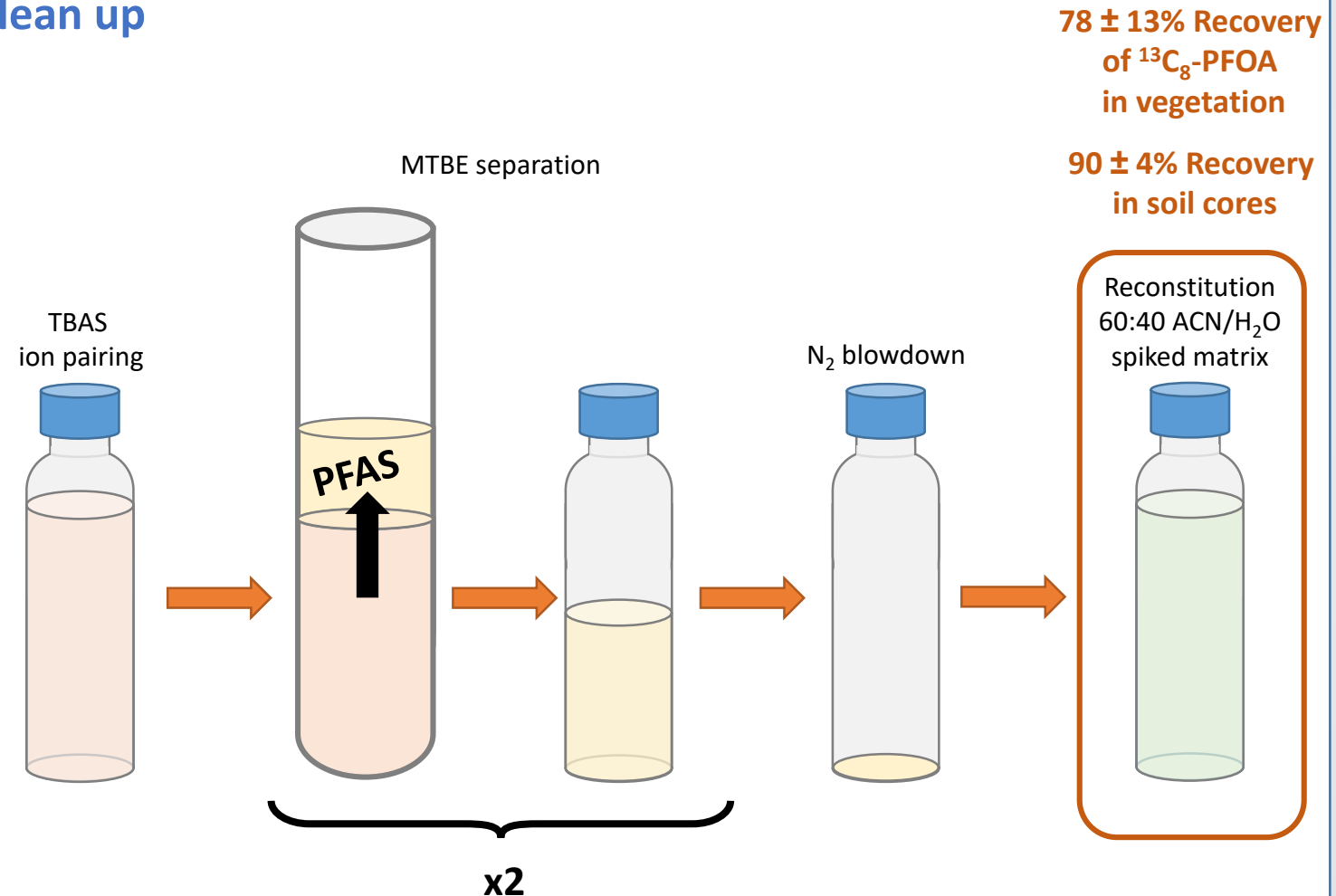
Partitioning of next-generation PFAS compounds in vegetation and soil cores

# Sample Prep: Vegetation & Soil Core Extraction

## Extraction



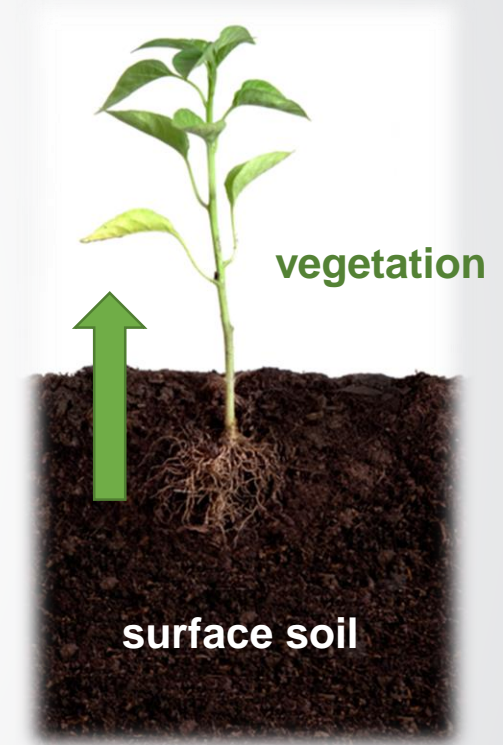
## Clean up



## Vegetation Accumulation Factor (VAF)

$$VAF_{[0,1]} = \frac{[[0,1]]_{vegetation}}{[[0,1]]_{surface\ soil}}$$

- Ratio enables comparison between different compounds

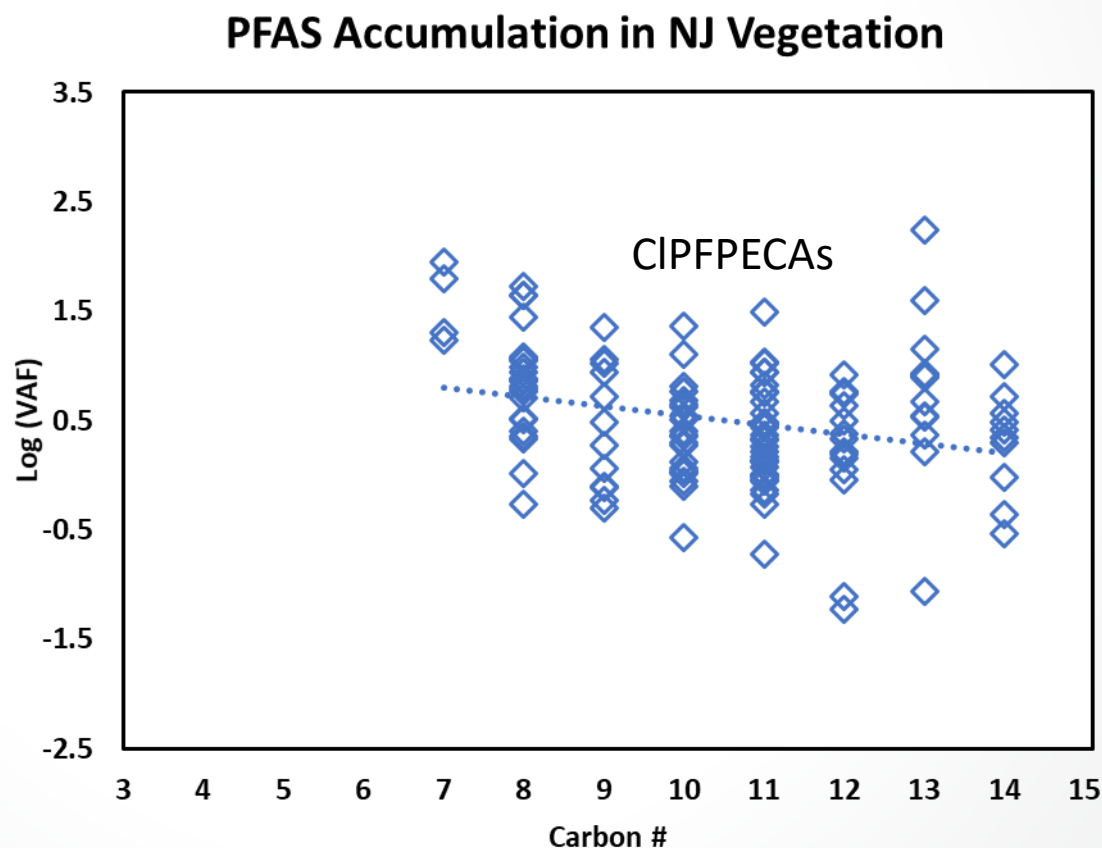


# Partitioning into Vegetation

## Vegetation Accumulation Factor (VAF)

$$VAF_{[0,1]} = \frac{[[0,1]]_{vegetation}}{[[0,1]]_{surface\ soil}}$$

- Ratio enables comparison between different compounds

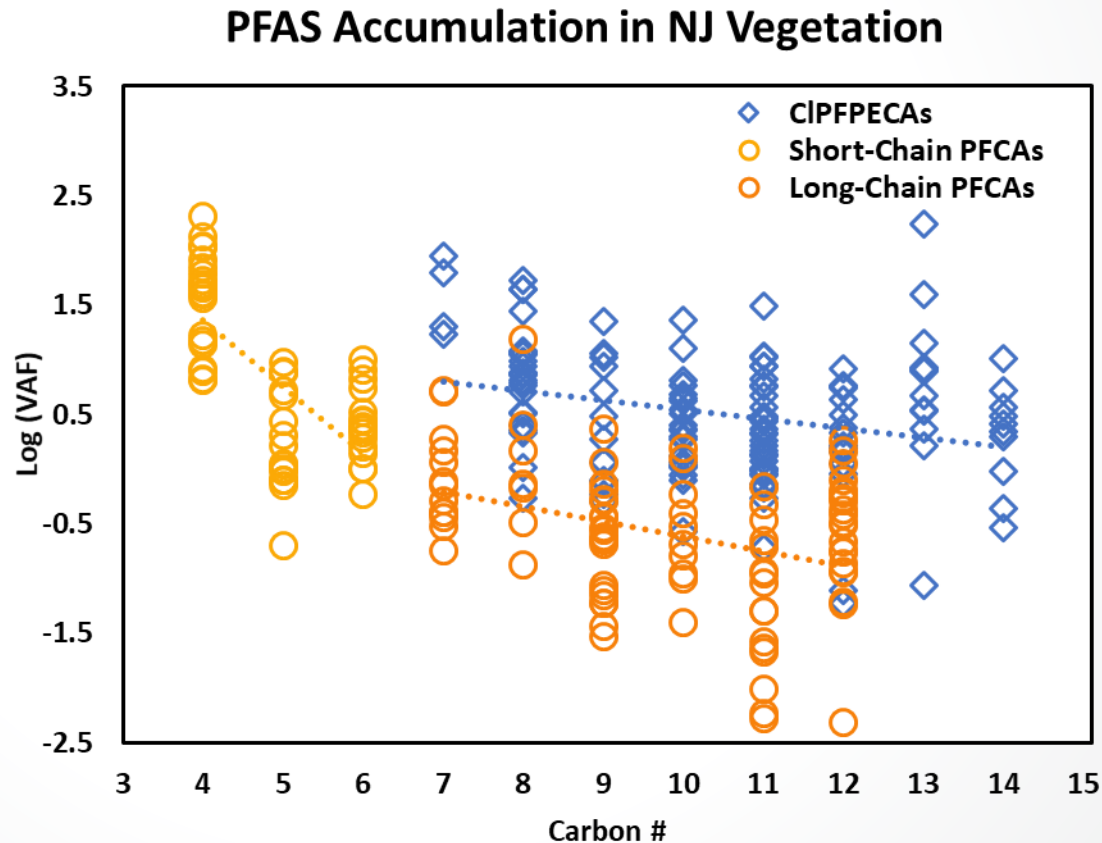


# Partitioning into Vegetation

## Vegetation Accumulation Factor (VAF)

$$VAF_{[0,1]} = \frac{[[0,1]]_{vegetation}}{[[0,1]]_{surface\ soil}}$$

- Ratio enables comparison between different compounds
- Short-chain PFCAs exhibit stronger trend with chain length
- Long-chain PFCAs and CIPFPECAs follow similar trend with chain length
- CIPFPECAs exhibit larger VAF than long-chain PFCAs





# Partitioning into Soil Cores

## Subsoil Accumulation Factor (SAF)

$$SAF_{[0,1]} = \frac{[[0,1]]_{soil\ core}}{[[0,1]]_{surface\ soil}}$$

- Ratio enables comparison between different compounds

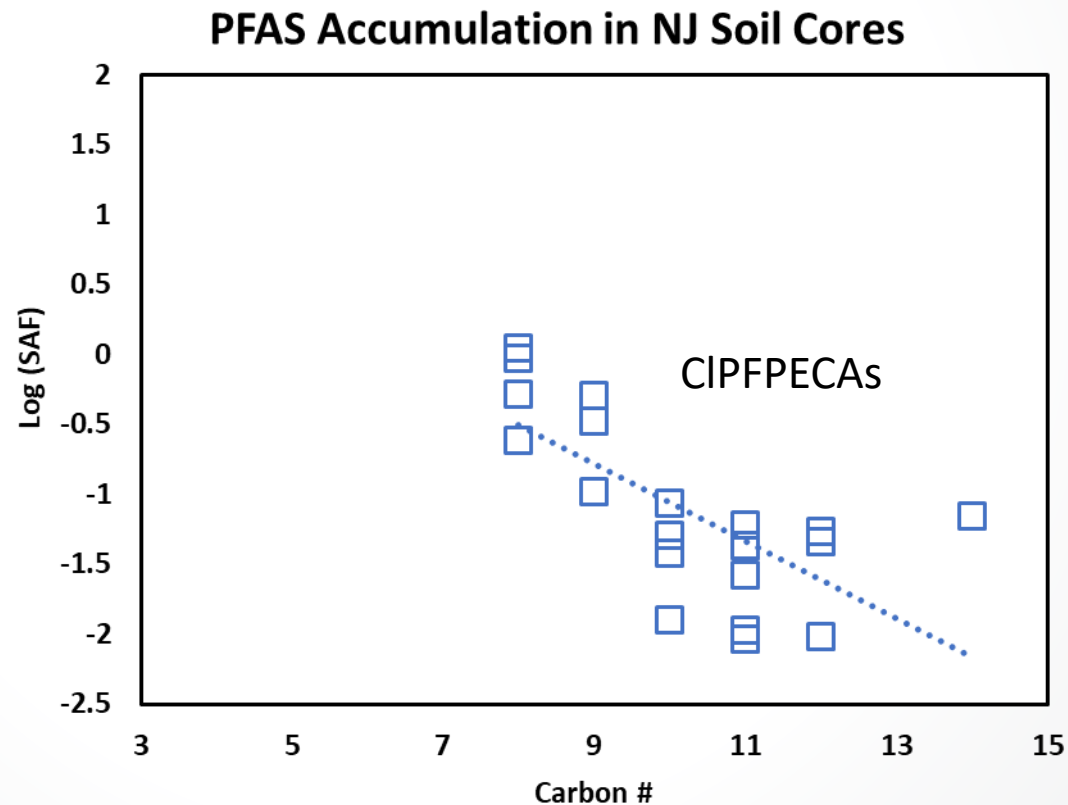


# Partitioning into Soil Cores

## Subsoil Accumulation Factor (SAF)

$$SAF_{[0,1]} = \frac{[[0,1]]_{soil\ core}}{[[0,1]]_{surface\ soil}}$$

- Ratio enables comparison between different compounds
- For CIPFPECAs, significant reduction in subsoil accumulation factor with increased chain length
- Multiple pathways for PFAS transport



Preliminary unpublished results. Please do not share.

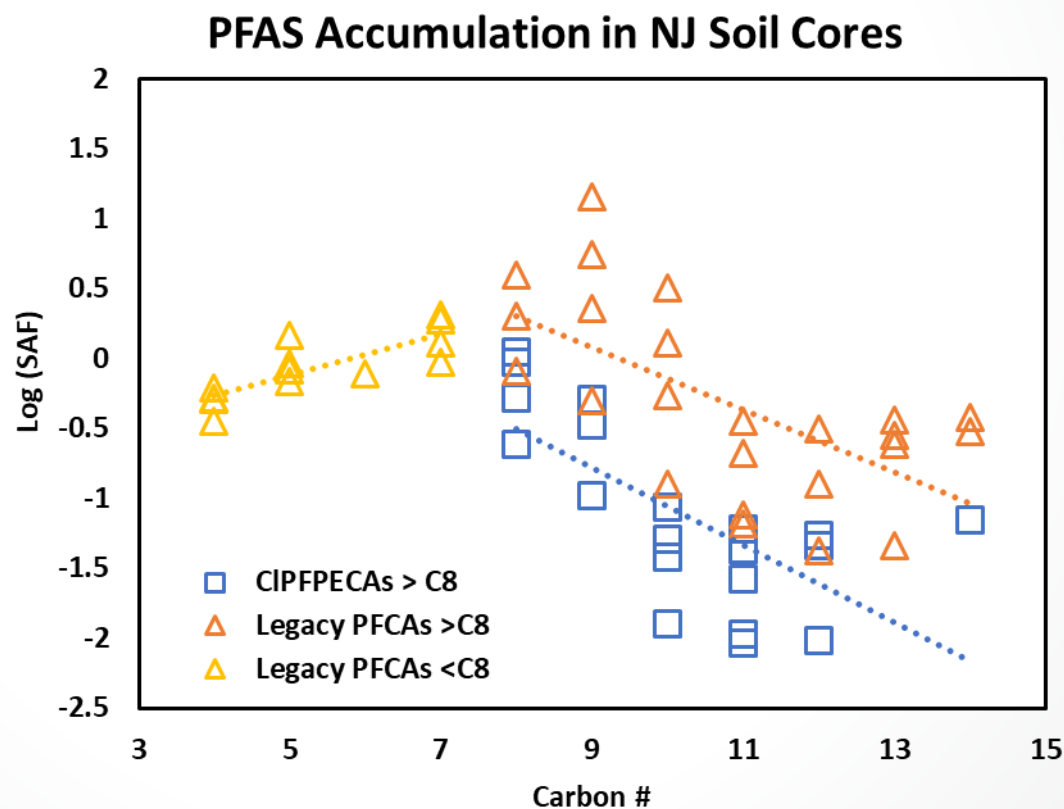


# Partitioning into Soil Cores

## Subsoil Accumulation Factor (SAF)

$$SAF_{[0,1]} = \frac{[[0,1]]_{soil\ core}}{[[0,1]]_{surface\ soil}}$$

- Ratio enables comparison between different compounds
- For ClPFPECAs, significant reduction in subsoil accumulation factor with increased chain length
- Multiple pathways for PFAS transport
- Legacy PFCAs show similar trend with chain length, but overall higher accumulation in soil cores
- Kinetics of transport important for interpretation



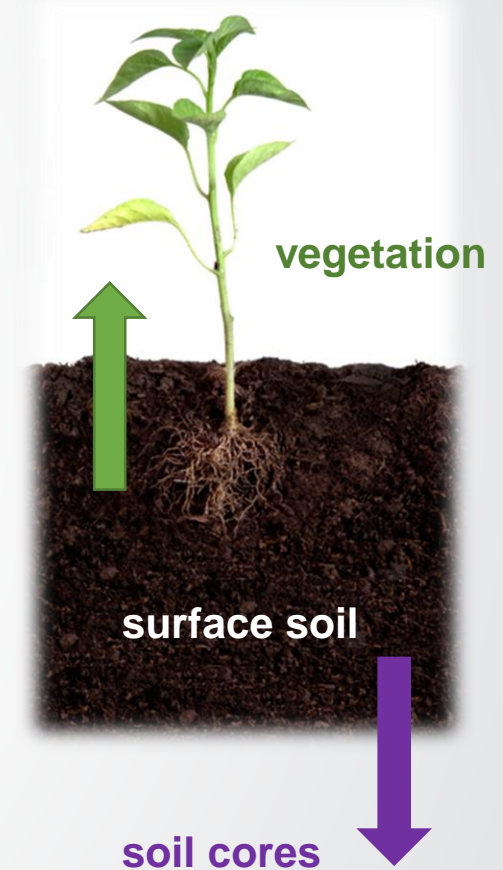
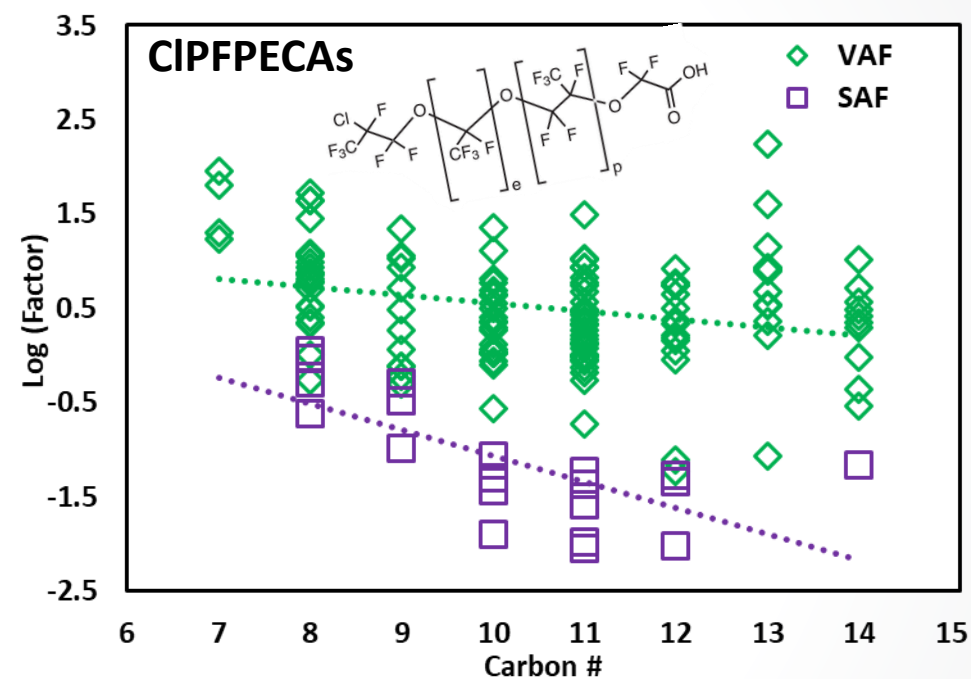
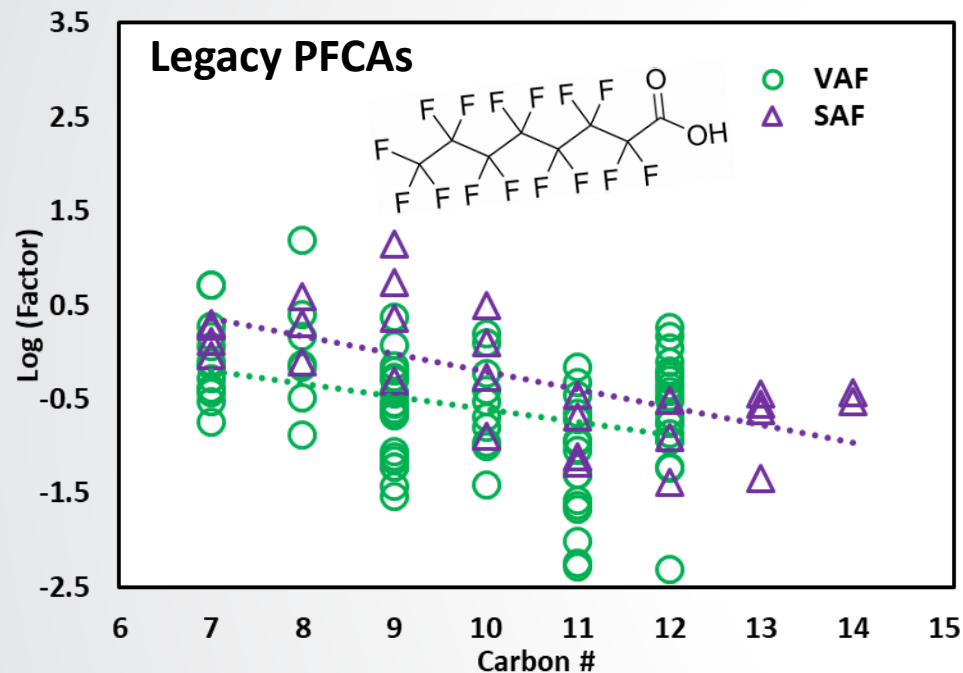
surface soil

soil cores



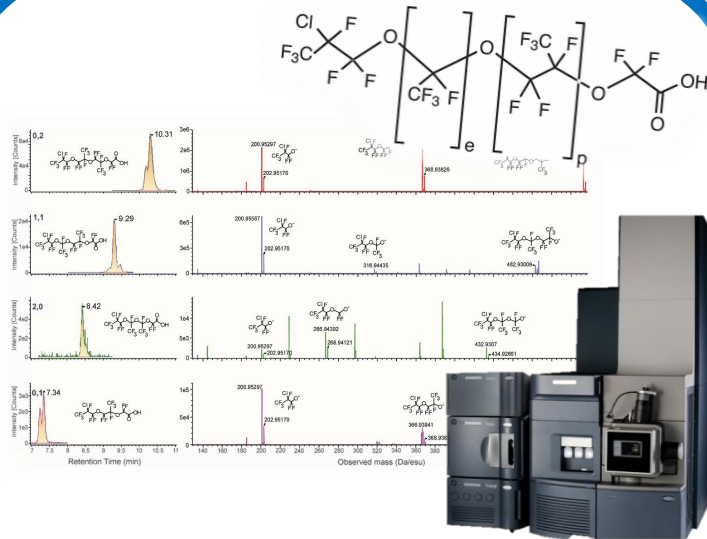
Preliminary unpublished results. Please do not share.

# Preferential Partitioning

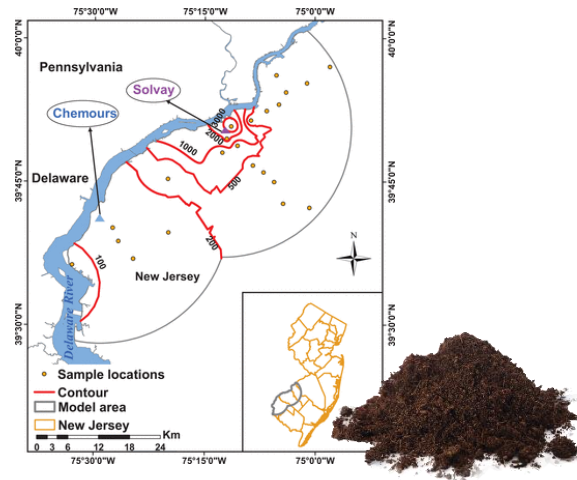


- Long-chain legacy PFCAs partition similarly to vegetation and soil cores
- CIPFPECAs preferentially partition to plants over soil cores
- Better understanding of pathways and kinetics of transport necessary for interpretation

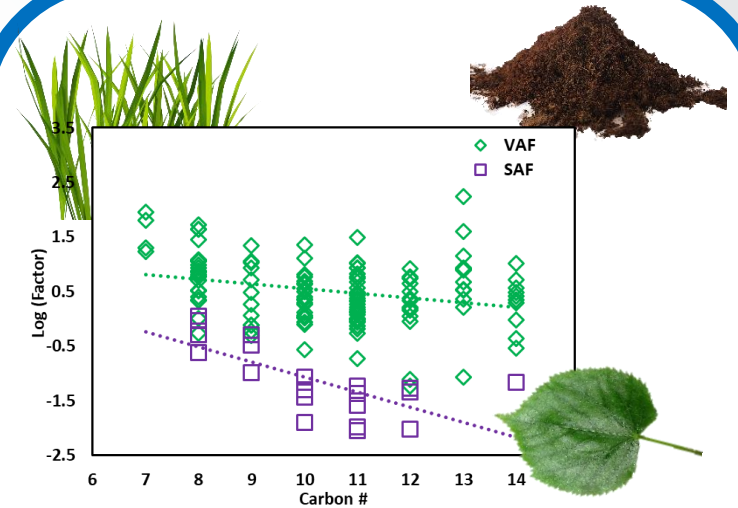
Preliminary unpublished results. Please do not share.



HRMS enabled detection of next-generation CIPFPECAs in NJ environmental samples



HRMS data informed method for semi-quantitation of compounds in environment



Partitioning of next-generation PFAS compounds in vegetation and soil cores

NTA is a launching point for informing future studies



# Acknowledgements

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# Questions?

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